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Prepared for

Robert S Kerr Environmental Research Lab, Ada, Okla

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16. ABSTRACT

The report contains the papers, questions, and answers from the Second Open Forum on managing petroleum refinery wastewater, held in Tulsa, Oklahoma, June 6-9, 1977. Forty presentations were made on the subjects of present and future regulatory and research direction; individual problems in wastewater management; the origin, interpretation, and problems in addressing the priority pollutants in the Settlement Agreement of June 1976; future considerations in biotreatment; powdered and granular activated carbon; and cost/benefit considerations. The invited speakers represented the USEPA, other regulatory agencies, the refining industry, the consulting and academic communities, and public interest groups.

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ON
MANAGEMENT OF PETROLEUM REFINERY WASTEWATER

Presented by

The U.S. Environmental Protection Agency

The American Petroleum Institute

The National Petroleum Refiners Association

The University of Tulsa

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The Second Open Forum on Management of Petroleum Refinery Wastewater was held at the Sheraton Inn-Skyline East in Tulsa, Oklahoma. This four-day (June 6-9, 1977) symposium was sponsored by the U.S. EPA in the form of Grant No. R804968-01-0 to the University of Tulsa. Fred M. Pfeffer and Francis S. Manning served as Project Officer and Project Director respectively. In addition, the American Petroleum Institute, the National Petroleum Refiners Association and the University of Tulsa contributed matching funds.

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Success of any project is aided immeasurably by support "from the top." Such support was provided enthusiastically by Arne E. Gubrud, API; Herb Bruch, NPRA; Bill Galegar, EPA, Ada, Oklahoma; and J. Paschal Twyman, University of Tulsa.

Of course the speakers' contributions cannot be overestimated. Not only did they present most knowledgeable and timely papers but they also reviewed the resulting discussions.

The Project Director and Project Officer regret that it is impossible to identify all of the numerous colleagues and friends who contributed so much to this symposium. However special thanks are due to Katie Whisenhunt, Shirely Clymer, Cathy Whisenhunt, and Cathy Clymer for managing the registration and typing the proceedings; Ed and Dan Andrews for tape recording the proceedings; Nelda Whipple for transcribing the tapes and typing the proceedings; and John Byeseda for photographing the speakers and session chairman.

WELCOMING REMARKS

William C. Galegar
Director, R.S. Kerr Environmental Research Laboratory
U.S. Environmental Protection Agency

Honored Guests, Ladies and Gentlemen...

As we assemble here for the opening of the Second Open Forum on "Management of Petroleum Refinery Wastewaters," I am reminded of a saying attributed to the French author, Alexandre Dumas. It is... "Nothing Succeeds like Success!"

In a sense, we will be challenging the truth of that statement during the next few days. As those who participated in the first Open Forum just over a year ago will recall, it was a very successful gathering. It clearly established the advantages of the exchange of technical information among the industry, academia, all levels of government agencies and the interested public.

The question is, what do we do for an encore? In welcoming you here, I want to sketch for you some of the efforts made by the hard-working committees putting the conference together to improve on the earlier product.

We have maintained the firm base on which the first meeting was built -- the co-sponsorship of the Environmental Protection Agency, the American Petroleum Institute, the National Petroleum Refiners Association and the University of Tulsa.

We have again brought together a group of outstanding speakers, each with specialized knowledge,. who will maintain the high level of technical excellence and the presentations last year.

We have directed our emphasis to a more specific objective, that of "Environmental Conservation in Petroleum Refinery Wastewater Treatment."

Finally, we have solicited the views of the Natural Resources Defense Council and the Environmental Defense Fund on the scientific rationale behind the differences which led to the courts and the consent decree. This, we believe, adds a new dimension to our forum.

Along with expressing the formal welcome to you...many attending for the second time...allow me to include the hope that through your active participation in the sessions we will prove beyond a doubt that Mr. Dumas was correct... that we will succeed in taking another big step toward our mutual goal of improving enviornmental quality.

BIOGRAPHY

William C. Galegar

William C. Galegar holds a B.S. in Chemical Engineering from Oklahoma State University and an M.S. in Chemical Engineering from the University of Oklahoma. His career has included 11 years with Oklahoma Department of Health and 16 years with the Environmental Protection Agency and its predecessor agencies. Mr. Galegar is currently Director of the EPA's Robert S. Kerr Environmental Research Laboratory in Ada, Oklahoma.

KEYNOTE ADDRESS

"WHAT DOES JULY 1, 1977, MEAN NOW?"

Joe G. Moore, Jr.
Head, Graduate Program in Environmental Sciences
The University of Texas at Dallas

It is good to be with you. I spoke to you in your prior conference as the Program Director of the National Commission on Water Quality, attempting to predict whether or not the Commission would recommend changes in Public Law 92-500. The Commission did make such recommendations. A year has elapsed since those recommendations were delivered to the Congress, and we now approach one of the critical deadlines in that statute. So that I have some knowledge of my audience, how many of you are engineers and consultants to oil companies? I see, mostly that. Alright, how many of you are lawyers? Any lawyers? Interesting. How many of you are oil company employees as opposed to consultants involved in water pollution control? Okay. How many of you will claim to be representatives of the Environmental Protection Agency besides Bill?

I would like to focus primarily upon the question, "What Does July 1, 1977 Mean Now?", now that it is the first week in June. For some reason, there is a general feeling that that date is no longer significant since the deadline is almost gone. How many effluent limitations for best practical control technology currently available are final four and one-half years after the passage of Public Law 92-500? How many permits required to have been issued under P.L. 92-500 are now coming to the end of their five year terms? What has been the effect of the extensive litigation with regard to the concepts involved in P.L. 92-500, particularly as related to July 1, 1977, as the answer to that question might bear upon the requirements of July 1, 1983? You see, this statute is reaching the mid-point in its first ten year plan, and the question is, "Where are we, and where are we going?"

I would like to review first of all the fundamental concepts that 92-500 requires effluent limitations as the basis for permits under the NPDES (the National Pollution Discharge Elimination System). Effluent limitations are the basis for permits for every single point source discharge in the nation. The backbone of the Act is really in sections 301 and 304 which prescribe the promulgation by the Environmental Protection Agency of "best practicable control technology currently available" and "best available technology economically achievable," the effluent limitations upon which permits are supposed to be based. The first U.S. Supreme Court decision, du Pont I vs. Train, has been decided with the opinion that the approach of the Environmental Protection Agency in developing single-number effluent limitations is valid. The court also bridged the gap between the different appeals procedure for sections 301 and 304 in such a way as to validate what EPA had thus far done with their effluent limitations approach. In addition, the court held that it is appropriate to issue single-number effluent limitations as opposed to a range of numbers as had been argued is actually required by section 304. The effect of this ruling is to validate the approach used by the EPA in the promulgation of effluent limitations. It was also held appropriate that the agency issue not only the guidelines under section 304 but the effluent limitations under section 301 simultaneously. In the final analysis, EPA has won one of the most crucial issues to the application of P.L. 92-500 even though their record of litigation in most cases has not been that outstanding. The other sections that do require effluent limitations or provide some basis for permitting conditions are section 306 for new source performance standards, section 307 for toxic and pretreatment standards, and a section that has been often overlooked, section 302 which requires that the Administrator issue effluent limitations for water quality standards achievement for those waters which have been characterized by the EPA as water quality limited. To my knowledge, the Administrator of EPA has issued no effluent limitations for the achievement of water quality standards described in section 303 with the effluent limitations detailed in section 302. The reason I mention that particular procedure is because, in my view, that may come to be one of the more critical provisions of P.L. 92-500 as we move past July 1, 1977.

Let me digress for just a moment, to mention the Congressional issues, or the legislative issues, with which the Congress has contended since the National Commission on Water Quality made its recommendations. I shall mention the ones that I regard to be crucial in judging what Congress may do. First of all, the construction grants program is running out of money; that is, the construction grants program for municipal wastewater treatment plants. There are several states which will have, before this calendar year is ended, committed or obligated all of their shares of the $18 billion originally authorized in P.L. 92-500. That means that some action either must be taken by the Congress to provide additional funding for construction grants under P.L. 92-500, or the publically owned treatment works construction grant program will grind to a halt in some states. One of the crucial states in which the construction grant funds will be exhausted is Maine. Section 404, which allows the Corps of Engineers to issue permits for disposal of dredged materials into navigable waters and adjacent wetlands continues to be controversial in the Congress, with a wide divergence between the viewpoints of the Senate Subcommittee of the Environment and Public Works Committee and the House Public Works Committee; that issue remains unresolved. On the House side, the Members have expressed continuing interest in decentralization of the program, or what has come to be known as certification to the states for various activities required under the Act. I think the House will continue to be interested in that particular issue. There was an effort to extend the July 1, 1977, deadline so that is an issue or was an issue in the legislation that has been considered twice by the Congress in the last 15 months. There is also the continuing question about what to do with the 1983 deadline and whether or not that deadline should be extended. These represent what to me are the major issues; probably the two critical ones are the question of any extension of deadlines and the money for construction grants. I regard section 404 as a peripheral issue to the general thrust of the water pollution control program; nevertheless, it does provide a basis for disagreement between the Houses.

When Congress adjourned in the fall of 1976 there was pending legislation to amend the pollution control act. It was in conference committee between the two Houses, and there was rather a stormy session at which there was substantial disagreement between Congressman Jim Wright, then the ranking majority member on House Public Works, and Senator Muskie, Chairman of the Subcommittee on Environmental pollution. At that time, apparently the conferees adjourned and decided not to meet again, or at least did not have an opportunity or occasion to meet again. The bill was stalled, in any event, by the filibuster then occurring on the Senate floor over the amendments to the Clean Air Act of 1970. Thus the congressional session ended with major disagreements over the general thrust of both air and water pollution control legislation.

With the change in Administrations and an emphasis on the need to stimulate the economy, the Senate Public Works Committee again, through a device designed to provide money just for construction grants, precipitated a parlimentary issue in such a way as to frustrate the legislation amending 92-500. The sequence of events is complicated because the water pollution control program became intermingled with the question of economic recovery in such a way that it was sometimes difficult to determine just exactly what was happening. Senator Muskie succeeded in having added to the Administration's jobs bill an appropriation to continue the construction grants program for a year. Since this issue represents one of the major questions in the amendment to P.L. 92-500, had that appropriation remained in the jobs bill, then some of the leverage which the House felt was essential in the consideration of other amendments would have been lost to the House. When the jobs bill was returned to the House where it had originated, the appointment of conferees from the House was delayed. In other words, the jobs bill which had originated in the House had gone to the Senate where this amendment had been added and then the bill had been returned to the House for the appointment of conferees. Had the House gone immediately to conference, they would have been confronted with the situation in which all they could attempt to do would be to eliminate the $4 billion authorized and appropriated for construction grants for publicly owned treatment works. Faced with that alternative, the House decided that they would proceed in such a way as to precipitate amendments to 92-500 into the conference on the jobs bill; thus, the appointment of conferees was delayed until the House passed a bill amending 92-500 and covering some of the points I mentioned a moment ago, as well as others, that are in controversy between the two Houses. The House then appointed conferees with both the jobs bill and the House amendment of 92-500 in the same conference. So the conference began. Initially, the House proposed that the question of construction grants authorization be separated from the jobs bill and the jobs bill be agreed upon and sent back to both Houses for passage and thence to the President. The Senate declined. After several meetings Senator Muskie, apparently concluding that there was no chance of the construction grants appropriation surviving in the jobs bill, finally agreed to the original House offer. The House dropped consideration of any amendments to the jobs bill that would relate to 92-500, and the Senate accepted the deletion of the appropriation for construction grants. Where that leaves the water pollution issues is that the House-passed bill is now theoretically pending in the Senate, but there is a question as to whether the Senate will actually consider that piece of legislation.

Senator Muskie called hearings beginning this week in several cities across the U.S. and extending them throughout the month of June, culminating in a series of hearings in Washington late in June on the provisions of 92-500. Unfortunately, the hearing cities do not afford real opportunity for participation. For example, one in Portland, Maine; one in Greeley, Colorado; one in Duluth and another in Alexandria, Minnesota; one in New Orleans, and one that was initially scheduled in Berkeley but has now been rescheduled, I understand, for San Francisco, with one other hearing at a place listed in the announcement as "undetermined," Iowa. Whether these hearings will produce a great deal of testimony remains to be seen. There will then be several days of hearings in Washington.

I have reviewed that legislative history, because I want to return to the fundamental question, "where are we with July 1, 1977?" For some reason everyone seems to think that we're so near the deadline that it doesn't make any difference. One of the reasons I asked whether there were lawyers here is because I think the lawyers are going to be very busy in the month of July. And if your clients or your employers are not in compliance with permit conditions on July 1, 1977, I would suggest that you call your lawyer's attention to the fact that they should be prepared to respond to litigation shortly after July first. I'm in a minority in what I think is likely to happen, I know. It is very difficult to predict; quite frankly the closer we get to this date, the more difficult it may be to predict, exactly what will happen.

Just let me mention some choices that are available to the Administrator of the EPA. When I talked with Bill Galegar about this appearance, I told him that the title of my remarks was going to be, "What Now, Brown Cow?" Because the question is, "What now, Mr. Administrator of EPA?" Of course, one alternative is to do nothing and just let things proceed as they have been proceeding, with no change. Another possibility is to selectively institute enforcement proceedings in the courts against industrial dischargers. Pick out the horrible examples - - and the chances are, if this is the course that EPA has under consideration, undoubtedly U.S. Steel will be at the top of the list. There may be some oil companies close behind. What I'm saying is that the Administrator could selectively choose against whom the law would be enforced and, in this alternative, institute no actions against publicly owned treatment works, that is, municipalities. Everyone sort of shrugs and says, well, what can you do about the cities? Would it help to put Abraham Beame in jail? It might help Bella Abzug, but I don't know that would help anyone else. Another alternative would be to selectively enforce, that is, pick some flagrant industrial violators or recalcitrants and institute suit against them; do the same for some selected municipalities, hopefully municipalities with Republican mayors or Republican administrations, so that you could get even with those actions which were instituted under the Republican Administration against some of the larger cities in the country. Here again, this is a selective alternative; the Administrator picks those against whom he would enforce. Another alternative would be to continue the procedure of ECSL letters. If you haven't seen an ECSL letter, or don't know what this means, it is, in effect, an administrative device for selective extension of the July 1, 1977 deadline - - an administrative device, you will notice. This procedure was roundly criticized publicly by Senator Muskie and staff of the Senate environmental Pollution Subcommittee as being illegal under 92-500 and might now be characterized as a Republican dodge of the intended effect of the statute. Quite frankly, I think it's illegal. I do not believe that it has support in the statute, and, therefore, I think those who go this route may find difficulty if the courts, as one court already has, hold it an invalid application of 92-500. By the way, EPA may still be thinking that the ECSL letter offers a means of doing something about the July 1, 1977 deadline.

Of course the real alternative that, in my view, is mandated by the statute is the filing of suits against every point source discharger in the nation that is now, or will be on July 1st, in violation of the law. Regardless of whether it is a practical solution or whether it offers any real chance in terms of being seriously considered administratively, in my view, this is what the law requires. The objective would be to secure as rapidly as possible consent decrees in the courts spelling out the conditions under which dischargers would comply with the requirements for July 1, 1977.

You should be aware that the EPA is, however, approaching industrial dischargers with an unusual question as a basis for determining penalties, "how much money have you saved by not installing 'best practicable control technology currently available'," or, to put it differently, "what would you have had to spend had you timely complied with the requirements by July 1, 1977?" This concept of the appropriate penalty is one that was embodied in the proposed revisions to the Clean Air Act of last year and will undoubtedly be, in my view, proposed by the Administration in any recommended changes to 92-500. The argument is that collecting a penalty equivalent to what the discharger would have had to spend will somehow restore equity between those who have complied and those who failed to comply. If you are now involved in litigation, you may as well tell your lawyers to be prepared - - and you might as well begin to try to figure what the cost would have been if you had complied with the statute - - because I think this will be an issue, at least in the discussions of settlement of pending litigation.

The last alternative that I have identified is the Administrator could ask for Congressional relief. Frankly, this appears to be very unlikely at this point in time. The controversial issues in 92-500 are interlocked in such a way that it would be very difficult to solve any single one of them, as the Senate learned by trying to put construction grants money in the jobs bill; it is very difficult to take any single one of them and isolate it for statutory amendment.

How would you like to be faced with the alternatives I've suggested? For some reason, the impression has grown that if we can just get past July 1, 1977, it will go away. I don't think so.

There are a series of statutory provisions that are interlocked in such a way that you cannot plan with very much certainty what may happen in an individual case. I'm just going to read a sentence or two from the series of these. Beginning with section 301 - - and sometimes we overlook these kinds of provisions because they're stated right in the front of the section and we don't get around to them because we focus upon the substance of a provision - - section 301 starts out by saying, "Except as in compliance with this section and sections 302, 306, 307, 318, 402, and 404 of this Act, the discharge of any pollutant by any person shall be unlawful." Now, the sections cited are section 301, the one under which the Administrator prescribes general effluent limitations for 1977 and 1983; 302 is the section that requires effluent limitations for water quality limited waters; 306 is the section that prescribes new source performance standards; 307 requires toxic and pretreatment standards; 318 contains a special provision on aquiculture; 402 is the permit section; and 404 governs the disposal of dredged spoil to which I referred earlier. I'm going to read the first sentence of 402, "Except as provided in sections 318 and 404 of this Act, the Administrator may, after opportunity for public hearing, issue a permit for the discharge of any pollutant, or combination of pollutants, notwithstanding section 301 (a), upon condition that such discharge will meet either all applicable requirements under sections 301, 302, 306, 307, 308, and 403 of this Act, or *prior to the taking of necessary implementing actions relating to all such requirements, such conditions as the Administrator determines are necessary to carry out the provisions of this Act*." (Emphasis added.) What that provision says is that if the Administrator for some reason has not done what he's required to do under those sections - - 301, 302, 306, 307 and so on - - he may require "such conditions as the Administrator determines are necessary to carry out the provisions of this Act." Since the Administrator has not prescribed effluent limitations under section 302, and even though the effluent limitations under section 301 and 304 have not become final - - nor have those for new source performance standards or toxic pretreatment standards - - the Administrator may apply such conditions as he deems appropriate to achieve the objectives of this statute. At the end of that same section 402, there is a provision, subsection (k), which says, "compliance with a permit issued pursuant to this section shall be deemed compliance, for the purposes of sections 309 and 505, with sections 301, 302, 306, 307, and 403, except any standard imposed under section 307 for a toxic pollutant injurious to human health." Thus, if you have a permit that has been issued by the Administrator or the state acting under delegation of the NPDES authority, then that does comply with the law. The permit contains the bottom-line conditions. It is true that the permits may expire as late as 1979, so that your client or company may not be confronted with a permit to be reissued this year or during the next year or so. Remember, however, that a violation of the permit is a violation of the statute, so, if there is any evidence that a permit is being violated, either as to the completion of the waste treatment facilities or the actual parameters contained in the permit, the discharger is subject to enforcement action under the statute.

One of the "hookers" about which no one is certain is the application of section 505, the first provision of which reads, "Except as provided in subsection (b) of this section, any citizen may commence a civil action on his own behalf, (1) against any person (including (i) the United States, and (ii) any other governmental instrumentality or agency to the extent permitted by the eleventh amendment to the Constitution) who is alleged to be in violation of (A) an effluent standard or limitation under this Act, or (B) an order issued by the Administrator or a State with respect to such standard or limitation, or (2) against the Administrator where there is alleged a failure of the Administrator to perform any act or duty under this Act which is not discretionary with the Administrator." The effect of that provision is to say that even if the Administrator of the EPA determines that he will not, on behalf of the U.S., institute enforcement action against a violating discharger, any citizen may institute action not only against the violator but against the Administrator for failure to execute the provisions of the statute in those cases where he does not have discretion.

I haven't read the statutory provision describing enforcement, but that provision very clearly says that, when the Administrator becomes aware of a violation, he shall - - not, he may - - but he shall institute proceedings. At the risk of being proved wrong in less than a month, I say again, you had better advise your lawyers to be prepared for litigation, if you are in violation of any part of an existing permit.

I will outline what could be, I think, a realistic chain of events. First of all, any Administrator subject to confirmation has to commit himself to enforcing the law. Can you imagine a question in a confirmation hearing where a Senator asks a prospective administrator, "what do you intend to do about the July 1, 1977 deadline?" If the Administrator wishes to "pass muster," he almost has to say, "I will enforce the law." Of course there is a difference between a confirmation hearing and July 1, 1977, but the issue will remain on July 1, 1977. The Administrator has taken an oath to enforce the statute. If the EPA decides that they will selectively enforce, either against industrial dischargers or against a selected group of industrial and municipal dischargers, in my view, it will merely be a question of time until they are compelled to file suit against every discharger in violation of permit conditions. Whichis to say, they may begin with the intent that they will selectively enforce the statute, but it will merely be a question of time until events will lead them to be compelled to file litigation against every person they know to be in violation of 92-500. No one could publicly argue that somehow or another it is alright to enforce the law against one discharger that is in violation and not against another discharger that is in violation; there would likely be a public outcry. Remember also that it merely takes one person - - wherever the violating discharges are occurring, it only takes one person to decide that they will litigate against the discharger and the Administrator simultaneously and, presumably in the same litigation, if they wish to bring a violating discharger to account. Thus, you are confronted with that possibility from the outset.

I've concentrated primarily upon what I regard to be the major regulatory issues that not only the petroleum industry but also all industries will face on July 2nd, that is, what do you do about your permit conditions if you are in violation? Now of course, you can solve this problem by saying we are 100% in compliance and then you don't have to worry about the possibility of litigation.

I'm supposed to say something about research, so let me just add one or two words about that topic. First, nobody yet knows how much sludge we are going to generate or how many residuals we're going to have all across the U.S. from all these water pollution control efforts. If you're involved in a research area, sludge is one of the areas on which you should concentrate. The next major issue, in my view, will be the identification and control of non point sources. Another is, if we can reduce the volume of water being used in such a way as to close the cycle, I think more and more in the future the emphasis will be on closed cycle systems. Water reuse will continue to be critical and is highlighted by such episodes as are now being experienced in California. Probably, the most critical approach to research, however, is to design production processes to minimize the generation of pollutants. If you really want to be on the leading edge of the future in water pollution control, concentrate on the production process rather than the end-of-the-pipe, or minor modification at the end-of-the-pipe, processes for waste control. Those firms which manage to design processes that are specifically intended to minimize pollutants will be the ones that have the business in the future.

DISCUSSION

J. Dewell - Phillips Petr. Co. - In those states where they have requirements more restrictive than EPA where those states do not in themselves have delegated authority but those restrictive requirements have been written into the EPA permit, to what extent will EPA act to enforce those more restrictive state requirements?

Moore - Let me see if I can restate the question as I understand it. In those states in which there are water quality standards which require stricter levels of treatment than the effluent limitations prescribed by EPA and the conditions are in EPA permits, to what extent is EPA likely to move to enforce those permit conditions? I'll hazard a guess. I don't think EPA has yet seriously considered the problems of enforcement generally so I don't think that they fully appreciate the question yet. My guess would be that EPA will not move initially to enforce to achieve water quality standards fixed by the states so much as they're likely to move to enforce against those who have violated permit conditions under the effluent limitations of 301 and 304, which is to say that I'm not sure that EPA will assign very high priority to enforcing water quality standards. You may recall that in the summer of 1976 the then EPA Administrator went to the Congress with a recommendation that federal assistance for publicly owned treatment works for levels of treatment beyond those required for secondary treatment in 92-500 be withdrawn. That is to say, they were suggesting that the Federal government's interest should be restricted to a minimum level as prescribed at the federal level rather than that prescribed by the states. So, I don't think, offhand, that they'll move to enforce in those areas where they have water quality standards. Does that answer your question?

BIOGRAPHY

Until May of 1976, Joe G. Moore, Jr. was Program Director of the National Commission on Water Quality, the agency created in the Federal Water Pollution Control Act Amendments of 1972 to analyze the technological, economic, social, environmental and institutional imparts of PL 92-500. He is presently Head, Graduate Program in Environmental Sciences, The University of Texas at Dallas. Mr. Moore has had some 20 years of governmental service including Chairman, Texas Water Quality Board, Executive Director of the Texas Water Development Board, Administrative Assistant to Texas Governors Connally and Daniel, and Commissioner of the Federal Water Pollution Control Administration, Department of Interior, directing the national water pollution control program before the creation of the Environmental Protection Agency. He is a graduate of The University of Texas at Austin with bachelor's and master's degrees in government.

SESSION I

REGULATORY AND RESEARCH DIRECTION IN U.S. EPA

Chairman

William C. Galegar

Director, R.S. Kerr Environmental Research Laboratory
U.S. EPA Ada, Oklahoma

Speakers

Lamar Miller
"Toxic Strategy Overview"

Marvin L. Wood
"EPA's Research in the Refining Category"

"TOXIC STRATEGY OVERVIEW"

W. Lamar Miller
Effluent Guidelines Division
Environmental Protection Agency

Good morning, it is very nice to be here today. I am not sure whether I am a designated hitter or a pinchhitter. I guess the effect is really the same. Mr. Schaffer does indeed send his apologies for being unable to be here. He is participating in a command performance this morning and tomorrow on some of the very topics which Joe Moore has just been discussing with you. Most specifically, the agency's suggested input for midcourse corrections which the agency would like to recommend to the Congress in the very near future, as they relate to P.L. 92-500. I think that may be a sufficiently good excuse for his inability to be here today. He did want to be here. I'll try to do my best this morning to try to tell you the same story that he would tell you if he were here. I'll exempt most of the humorous remarks from that qualification. I don't think that Bob would use the same stories that I would tell you, but the serious part of the speech will be close.

I'd make one observation on a remark that the keynote speaker just made. It somewhat puts me in mind, Bill, of a cartoon that I keep pinned to my wall to remind me of our actions. Joe Moore's remarks about the approach used to evaluate the cost for implementation of BPT. The cartoon on my wall is two cavemen talking to one another. One says to the other in a very philosophical note, "Our future is shaped by our past, so be careful what you do in your past."

Be mindful that the estimated cost for the installation may also become the amount of the fine if the installation is not made. Very soon after the Supreme Court decision was announced I called up a friend in industry and said, "congratulations Bob, your corporation's name will go down in history as the first major loss in the water fight. That case will be known forever as the du Pont case. And, by the way, what did industry win on the appeal? Hadn't you really rather that you had lost some of them and therefore kept the old rules instead of the directions that you hope I'll tell you about today?" I think we ought to keep some of these thoughts in mind as reminders and go back and look at the 1976 meeting out here at Tulsa. I looked at some of the remarks which were made by the keynote speaker last year, as a matter of fact, Bill Galegar said that participation and communication made for a successful meeting; and, he asked this morning, how are we going to improve on that success. The keynote speaker last year said that effective communication is a two-way street and cited Joe Moore on effective communication in saying, "we must not only listen we must hear what is said." And then a number of speakers proceeded to tell everyone at the meeting that comments should be solicited from industry. Industry should be heard. EPA should listen to the industry. EPA should know industry's viewpoint, then reminded the audience of what the courts had told EPA about the errors of their direction at that time.

Folks, at this meeting, this morning, I would like to point out to you that Mr. Moore was right about communication. We must not only listen but we must hear what is being said. Mr. Beychok was also right; that communication is a two-way street; but it needs to be pointed out again; it really is a two-way street. We have to listen to you. We want to listen to you. We're trying to listen to you. And we're scheduling a lot of time to sit around and talk to you and listen to you. But, it is a two-way street. While we're listening, please hear what we're saying to you. It works both ways. Nobody in this audience is any more tired, and I'm glad Joe asked how many lawyers were here. I didn't see but one hand go up, I might have been wrong, maybe there are more, but we are all technical people, let's think that way for a minute. None of the technical people in this room are any more tired of the adjudicatory processes than are the technical people at EPA. And the people in the effluent guidelines division are the people who are catching the bulk of that work effort. We don't encourage the adjudicatory system; we don't want it; and, the directions are sufficiently different at this time that I don't think it is going to be as necessary. Communication, and every time I think about the topic I am reminded of a good Polish joke, a good Polish joke is a joke told to me by Polish people, I'm not one of the government employees who wants to get hung by the ethnic joke problem. I've no interest in telling that type of joke. But, it does reflect both on politics and is a reasonable observation of the problems of communication. It seems that in that great hall up in the sky, once upon a time, Lenin, the Czar of Russia and Napoleon were reviewing history as they saw the problems that they had in their political life and the problems in Poland today. Poland's problems were very much in a political discussion last fall if you remember, Lenin observed that if he had had the ability to control communication and what people understood as a result of mass communication the same as the First Secretary of the Party in power during the 1960's uprisings in Poland, that he would have won the revolution in Russia in 1908, he wouldn't have had to wait until 1918. The Czar responded that if he had had the ability to control communications to the people the same as he had observed had been happening today in parts of the world, that no one would ever have heard of Lenin, and that he would still be the Czar. Napoleon responded that if he had the ability to control communications and what people heard and what people understood as was done by the Polish First Secretary, that he would be convinced today, that after all, he had, in fact, won at Waterloo. I sometimes think that most of us hear and most of us listen to just about what we want to hear, and that means both EPA and industry. We're really trying to change that in the effluent guidelines division. We're really trying to change it at EPA. Remember that if we both go that extra mile it will make it a lot easier to make it a two-way street. We've got to both make the extra effort to listen and to talk. I believe that this group, represented by refiners and people associated with them, can really make that possible. I don't believe that it is necessary for either of us to prove that we are willing to go to court, we've already done that. I hope that it isn't necessary for us to prove to each other that we are failing by having to go to court. We've both done it enough times to know that we're willing to go back if necessary but I hope that we can avoid it by learning that it is unnecessary. Technically we can resolve our next series of issues. We're both going to have to learn to listen to both sides and we're going to have to both learn to go both ways on a two-way street. Let's not spend all of our time worrying any more about categorization, let's not spend it worrying about the semanic differences between limitations and guidelines. It was very interesting to me to hear Joe tell you this morning, that's settled. As I understand it, it is settled. The problem is, and our direction is, (this is very important to us and this is literally the most important thing in terms of the costs and economics of the effluent guidelines division right now), is to determine how best to do the regulations. By spending our money, and yours, in such a manner as to derive the greatest benefit for the environment for every dollar that is spent by us or by you. But we're not interested in spending money for the sake of spending money and we're not interested in deriving regulations for the sake of deriving regulations. We are interested in implementing the law as we understand it. It was once said by a famous English politician, Gladstone, the only thing "worse than a politician who thinks he has the truth up his sleeve is one who thinks God put it there." I want you to know that that particular observation is to me somewhat like the best advice that my father gave me (since Bill digressed into the good old boy storeis I think I will too). Dad looked at me once when I was just ready to finish college and he said, "son never argue with a fool in public, passersby can't tell the difference." I didn't recognize for twenty years that my father's remarks were really in fact a paraphrase of Justice Oliver Wendell Holmes' remarks published as an essay which he entitled, (I think fittingly for this particular group), "The Hydrostatic Paradox of Controversy", in which Mr. Holmes starts off by reminding us that if we had two pools of water, one the size of a soup bowl and one the size of an ocean, connected by a pipe stem, the levels of the water in each would be the same. This is very similar to the status of both wise men and fools engaged in controversy. The major difference being, the fools know it. The same is true of most of us; when we all get reduced to a common level of thinking that we have a noble exercise to go about, and no one can challenge or have any interest in adding to what we do. Now, you can put the last remark in perspective. I'll tell one more joke, current from the Washington scene about five men on an airplane. The pilot comes back and he says, gentlemen I have put this plane on automatic, I've come back to tell you personally that we have a real problem. This plane is not going to make it to the airport, and we're too far from any other place to satisfactorily land it. I know nothing else to do but tell you that we have four parachutes on board, and, unfortunately, there are five of us. You might think, as a general rule, since I am the captain of this ship, that I would give you each a parachute and allow you to jump while I stay behind with the plane. That, however, is not to be. I think that you should know that I work for the CIA and I have some very important information up in my mind that must get to the president tonight. So with that I am going to take my chute and jump out the door. I'll leave the problem to you. Another guy stood up and said; "gentlemen you may not think it's very important, I'm only an ex-president but it's very important that I survive because I still give continuous advice to the new administration, and I think that none of you would deny that I ought to have one of those chutes." With that he straps on a chute and jumps out the door. Another fellow stands up and he says; "I have been the Secretary of State and undoubtedly have been recognized overwhelmingly as the outstanding intellect of the world. I must be rescued for the benefit of all the world. My very being is very important; and with that I will leave"; and he jumped out of the airplane. There was left a hippie student and a minister. The student looks at the minister and he says; "father, I think that you should take the remaining chute." The minister looks at him and says, "no, son, you take it, you take it." The student looks around and he stirs around a little bit and says, "well I don't really think that we need to engage in this conversation." The minister looks at him and says, no, this is my life's work, to serve my fellowman, this is all I have to do, to make other people happy, you should take it and leave and I must make the sacrifice. I've had a long and healthy life and I've enjoyed it. You go and you save yourself." And then the boy looked back at him and he says; "but father, it isn't necessary for either one of us to make this decision; you see, the smartest man in the world just jumped out the door with my knapsack." I want you to know that the effluent guidelines division of EPA does not take the attitude that we are necessarily the smartest people in the world. We are neither going to jump out of that door with a knapsack, nor are we going to drive it straight into a wall. Joe pointed out, and I think well, that our litigation record was not too good. He's right. We intend that it's going to get a whole lot better. The reason for that is that we don't intend to issue regulations that we can't sustain. And if we can sustain them, I think you will probably be reasonably ready to agree with them. We may not have to have too much litigation in the effluent guidelines area. Now, to give you a reasonable overview of our toxics strategy, which is presumably what some of you wanted to hear from me.

On June 7, 1976, we entered into a settlement agreement which settled four cases brought against the agency by environmental groups. These cases were brought against the agency to force us to expand the list of toxic substances under section 307, to promulgate final standards for toxic substances already designated under section 307, and to finalize 8 pretreatment standards. I'm not going to discuss at length the details of the settlement agreement in as much as at least two other times during this conference it will be discussed by people who are more competent than me to discuss it. The materials that are dealt with under section 307a for which the final standards must be promulgated are pretty well known to most of you; aldrin, dieldrin, benzidene, endrin, DDT, DDE, DDD. The other materials which are identified in the settlement agreement have come to be known as the list of 65. Sometimes also referred to as the list of 129. Sometimes also known as the list of 543. Sometimes referred to as the list of 43,000. We will specifically delineate later in the meeting for you by another speaker from our division, exactly what the list really means to this industry. It is our attempt to try to focus your interest on specific materials. It's not going to continually change. We have identified 129 today. We hope that they will be satisfactory to do the job. The effluent limitations will be established on highly specific, technology based, limitations for 21 industrial categories identified in the agreement. At the risk of confusing this particular issue, also the 21 are now in fact 28, because miscellaneous chemicals which is one of the 21 is made up of 8 different categories. It's no longer 28, because one of them as of last week is settled and will be no discharge. The carbon black industry. That puts an end to one of the 28. The effluent limitations will be promulgated in the form of best available treatment economically achieveable for July 1, 1983. This particular work activity has become known as the BAT revision in the terminology of those developing effluent guidelines. We also sometimes refer to it as BATox, or BAT combined with toxic controls or priority pollutants. You may hear that term in the future. What that really means is best available treatment with priority pollutant control. These standards will also include pretreatment for existing sources, pretreatment for new sources and new source performance standards. The settlement agreement reflects the agency's strategy for handling toxic materials and other problem pollutants discharged into the nation's waterways. A number of control options are available to the agency and standards and regulations will be developed taking many of these options into account. The first step will be to establish technology based effluent limitations in a similar fashion as we did for previous effluent limitations, we don't expect to put any out that are not technically sustainable. If it is determined that these technology based effluent limitations are not sufficient to control the problem pollutants, the agency has the option of designating a particular material for coverage under section 307 and will not hesitate to do so. Under this section more stringent standards may be established without the detailed economic considerations as required in establishing effluent guidelines under sections 301, 304, and so forth. There is also the option of developing and upgrading existing water quality standards to resolve potential problems with specific materials of concern. You heard Joe refer to a little used section of the Act this morning. That particular sentence refers to the same little used section. It is an option available to us for the control of toxic materials. Specifically, the use of water quality standards to resolve specific problem areas. Our studies will proceed along slightly different lines than they have proceeded in the past. In fact the studies will proceed along lines which reflect the organization of the Office of Water Planning and Standards. We have four divisions and we have four study areas ongoing at the moment. Technical contractors will establish alternate levels of technology; and that is an important, perhaps new, consideration. We expect to have more than one level of possible treatment technology designated in the development of the regulations. These studies will look at the specific pollutants, i.e., the 129 priority pollutants and the traditional pollutants. Secondly, economic impact analysis as was done in the past will be a major factor and a major input to the overall study. Thirdly, studies to provide facts with regard to the impact of the designated priority pollutants on the aquatic environment will be conducted. Fourth, a study of the environmental mass balance of each of the materials will be conducted. This effort will look at the manufacture of the material, the movement of the material into various products and ultimately into the aquatic environment, and the source of the materials which do move into the aquatic environment. Each of the above factors will be weighed in determining the ultimate choice of technology and/or control options for preparation of regulations, not just technology and not just economics, but a mass balance and the effect on the aquatic environment. It is our intent, because of the complexities of all of these studies, to begin by screening specific industrial discharges and identified subcategories to determine the presence or absence of the designated priority pollutants. I made a short presentation to one committee of API, not very long ago, and within two days the Deputy Assistant Administrator got a telephone call that said; that I said at the meeting, we're going to have 129 regulations for every refinery. I don't know what I said that led the man to believe that, but I want to make sure that you don't go away believing that. The first thing that we are going in our technology based studies is to determine how many of the 129 are in fact a problem, and how many are not present in significant quantities, i.e., how many can we eliminate from being a concern from a particular industry or a particular category. This, hopefully, will allow us to narrow down the number of materials with which we have to be concerned in developing treatment technology. Once this has been done, we will proceed to quantify on a more extensive basis the significance of those materials that we found to be present, that is, how well does existing treatment handle those that are present and how many of those are no longer a concern. There will be some cases, for some categories, for some processes, where BAT is equal to BPT for one of several reasons. Either priority pollutants are not present, or the existing treatment renders them dischargeable in insignificant quantities, or they do not constitute a major source to the total aquatic environment, or mass balance studies indicates that the point sources under study do not constitute a major portion of the environmental impact of the pollutants. There are many reasons why any of these may not cause you a problem. Once we have quantified and made the determination that a material is present, and that it is present in an environmental significant quantity, then and only then will our efforts be concentrated on the selection of appropriate control strategies. As we proceed to develop these standards we will be opening up the process and will be inviting more active participation of the industrial community. We will again be soliciting data, and their assistance in areas of technology and its application to the problem. As a matter of fact, we have already begun soliciting assistance in technology application. We intend to let everyone know as best we can what we're doing and what levels of technology are under consideration at all times. We're going to play the entire scenario right on top of the table in the public view for all interested parties. We intend to use fully the authority that we have been granted under section 308 of the Act to gain information with regard to the various industrial categories on the specific materials of concern. We're also working very closely with industrial associations, not only this one, but others, in developing working groups, particularly in the area of analytical methods development and technology assessment. Of paramount importance to us is orderly and timely progress. In reading the settlement agreement one will notice that there are specific dates by which time certain portions of the job must be completed. The schedules are very tight. We will not have the time to provide leisurely reviews. Since we are opening up the process, soliciting cooperation and allowing everyone to know what we're thinking as we proceed, we feel that we can eliminate long review periods as well as a lot of litigation. Everyone is concerned with the discharge of problem or toxic pollutants and as good citizens everyone wants to control them to the maximum degree possible. We believe that as long as we proceed in a rational, cost effective manner, we will make progress together. We believe this to be the proper strategy for the control of the problem.

DISCUSSIONS

Pete Foley, Mobil Oil Co. - Can you give us an example of how economics will play a role in choosing the appropriate technology?

Miller - Yes, I can give you an example. Let me just try to describe a very specific case. Our Analysis and Evaluation Division will take the cost data associated with each technology level and evaluate it. There may be for instance a number of technology levels and an associated cost with each one. Obviously one level is no treatment. Another level may be, for instance, just an API separator. Another level may be an API separator followed by an extended aeration activated sludge system. Another level may be a bioplant combined with a filter, or combined with a carbon column within the process, or a carbon column at the end of the bioprocess. Each of those levels will be costed. Then the impact on the industry and the economy as a whole will be determined prior to determining the trade off or the benefit which we think is most cost effective. We will do this for a number of treatment levels for each regulatory action.

Milt Beychok, Consultant - I was interested in hearing you say that EPA would again use contractors to gather a great deal of the background information. They do that, and whether or not the EPA later, as they become more knowledgeable in the field, depends to a great extent on those contract reports I'm not sure. But they]re at least preceived by those of us in the field as being a data base that must be contested. Industry often ends up hiring their own contractor to prepare a rebuttal to the first contractor or to prepare cost estimates to rebutt your cost estimates. Has EPA ever considered opening up the process at the front end and gaining the review and approval of all interested parties in the selection of that first contract?

Miller - I'm not sure I really understand the question. I think that the answer is, no. I don't think that our administrative procedure allows the government to allow someone else to determine how they will contract for their business. There are some pretty stringent rules on what you go through to select contractors. Let me make one remark in regard to what you said about industry's general feeling or your general feeling about contractors. Let it be clear, at least from this day forward, no contractor writes regulations. I've seen that suggested in the past. The policy is pretty specific. All regulatory actions will be the specific responsibility of the appropriate project office and his supervision. The first level of regulatory recommendation we also changed as you will hear in a subsequent presentation by Bobby Dellinger. The system by which we review various levels of technologies, the costs, the associated economic review, the mass balance in the environment, and the rest of it has been put into what we call a working group. This group has some highly specific responsibilities. Bobby will discuss those with you in more detail, but let me just tell you that it's not going to be the work of a contractor that puts out a draft regulation for you to have to worry about.

It's going to be very easy for you to point a finger and say, this man is responsible for this exercise. We subscribe to that policy and it is the state policy of the new administration. You ought to be able to identify who it is and we're going to help you know who it is. It will not be a hidden contractor as it has been sometimes alleged to be in the past.

Milt Beychok, Consultant - I appreciate that, and I wasn't suggesting hidden contractors. I also appreciate that no one can participate in your selection of the final contractor in terms of the contract terms of price or scheduling. It might be well for the EPA to solicit from industry whom they at least consider competent enough to be on the original bidding list and who really does have experience in that particular industrial category. That was really all that I was talking of.

Miller - I have been in that position before; most specifically in the inorganic chemicals and the organic chemicals industries. Where industrial representatives said, "why don't you ask us who you should hire?" Which is effectively what you have said. I looked at the particular company that made the remark and asked, "Is your engineering division available?" "We know they are competent, we know they know how to design these processes, will you bid?" And the answer was, "no." It's not always that we don't get the people you want for us to have because we don't try. Mostly, it's because they don't want to get into government audit problems. The most recent case that comes to my mind is an extensive carbon column evaluation study where I asked a lot of people, everyone I know, who was qualified, please bid this time, please quit criticising us for the quality of our contractors when you won't even bid. And the bid list was not very long, and it was for quite a number of dollars. Yes, we have trouble getting good contractors; but the contractors we have, if we don't hold them to the line, don't blame it on the contractor. It's our fault. We have a job to supervise them and if we don't do it, it's our division's responsibility to come up and say, it's our ball. And we will this time. I think the one we have on this project is doing a very good job right now.

BIOGRAPHY W. Lamar Miller

W. Lamar Miller is the Chief of the Organic Chemicals Branch of the Effluent Guidelines Division. He has a B.S. degree from Mississippi College and an M.S. and Ph.D. in Chemistry with minors in Engineering from the University of Florida. He spent twelve years in teaching and industrial work prior to joining the Environmental Protection Agency in 1972.

EPA'S RESEARCH IN THE REFINING CATEGORY

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Actually, this is going to be more of an historical reminiscence than a current commentary on research the EPA is doing on refinery wastewater. For one thing, we haven't done any research since November; we've been working for Effluent Guidelines on a technical assistance project. Secondly, all the projects that we have any current interest in are listed later on in the program; thirdly, rather than chance saying something that would be corrected by a person who actually knows what they are talking about, I'm just going back in history and bring you up-to-date, partly from a philosophical angle, about what went on in the formulation of the research program and some of the results of our earlier projects. Actually, the reminiscing may be apropos since a Harvardian, a fellow by the name of Santayana, once observed that those who do not learn from the lessons of history are condemned to repeat them. Do we have the time or money to afford to repeat some of the lessons of history that we should have learned already, particularly in wastewater treatment and control in this specific industrial category?

For those who expected a more western philosophy here in the oil capital of, at least, the United States: there was once an Okie (not from Muskogee, but a little closer to here--the town of Claremore) who observed that all he knew was what he read in the newspapers, and he became rather famous for his comments based on that observation. Wouldn't Will Rogers have had a field day reading some of today's headlines in the newspapers? Especially with regard to aspects to the energy "crunch," "crisis," or whatever tag you want on it. Depending on which expert is being quoted, we may expect within the next one or two years to buy our gasoline in small goatskins, or at the other extreme, we might still be driving our gas guzzling V-12's by the year 2077 at a modest increase of X dollars per gallon for fuel. The truth, as usual, probably lies somewhere in between.

Where there are problems, there are ways to solve them. A technology as advanced as ours in a country that lives, moves, clothes itself, and produces its food from liquid hydrocarbon products can afford to give up this form of energy. We are not then in the position of holding a wake rather than forum or pondering over, for example, the wastewater treatment problems associated with buggywhip factories. Regardless of whatever source these liquid hydrocarbons are to come from in the future, they're going to have to be refined, and their changing characteristics will cause new wastewater treatment problems. I hope to cite herein some of the lessons of history so that we may avoid being condemned to repeat them in our future research and our future wastewater treatment and control efforts. With respect to the soothsayers of doom or utopia, some of the fairly recent economic projections were that there would be no shortage of crude because shale oil would be available in large quantities when the price of crude reached five dollars a barrel. Crude is not cheap, not plentiful, and not coming from shale. So much for soothsayers and oracles--one would almost be tempted to put them into a mythological category with demons, ogres, virgins, and dragons.

What is known at present, for example, is that there is more oil in known locations than we have consumed since Colonel Drake drilled his first well in Pennsylvania. Admittedly, there are problems in recovering this oil, since it has been subjected to primary production methods, and in some cases, secondary production methods. It is difficult to believe that a nation can afford to mine rocks on the moon but cannot develop technology to extract a little more of the crude that we know is there (and to a goodly degree, how much is there). Hopefully, we should be able to extract enough to give us some latitude until adequate stocks are available from exploration and new production, coal conversion or shale oil or even such "way out" things as hydrocarbon production from sunlight and cellulosic materials to make a new (and continuously renewable) source available. Admittedly, everything is finite and so are these potential sources of the "new crude." Nevertheless, until the little handy-dandy portable nuclear fusion energy generator comes along, we're going to have to learn to utilize them, and utilize them in a more wise fashion than we have in the past. America does live on liquid hydrocarbons; we have for seven decades, since the automobile and internal combustion engines were developed; and we are going to continue to, because we cannot replace overnight the transportation network that moves our fuel, our food, our fiber, our raw materials, and our finished products.

The situation does suggest that any new treatment options be regarded carefully since changing feedstocks are well known to have changing effects on wastewater effluent parameters (physical as well as chemical and biological) and the treatability there of. The answers to today's problems, as we see them now, are certainly not expected to be absolute. Until Woehler's synthesis of urea, chemists regarded organic chemicals as incapable of production by man--they were produced only by nature. Until 1903, the oil industry "knew" that there wasn't any market for aviation gas or jet fuel--there were no airplanes--how could there be a market? Until relatively recently, some of us who call ourselves sanitary engineers--and before I offend more people in the audience, I'm registered as one--anyway, some sanitary engineers just "knew" that the Imhoff tank or Emscher tank which removed the big pieces was going to solve water pollution problems. Then when biological treatment was developed, we "knew" that it would solve all the effluent treatment problems. We have been remiss in being so proud of the percentage removal figures; it's not what we took out that counts, it's what we left going back into the environment that has hurt us in the past.

If I may leave general philosophy, we can, with one dirty word, start concentrating on the background of refining wastewater research done at the Robert S. Kerr Environmental Research Laboratory (RSKERL). The dirty word is "matrix"; that word was "out" not too long ago, maybe it will be "in" again by tomorrow; but it fits this situation. If you will consider the number of control and treatment options that are available for effluents in general, you will find that it presents to a rather complicated listing. For example, select a number of simple headings for a series of columns--such things as chemical, physical, biological, and reuse/recycle. Now picture anyone of these headings and list the number of past and present treatment options that are available. Let's pick biological. Most of us are principally concerned with nominally aerobic processes, but there are also anaerobic processes, and in addition, there are some facultative treatment schemes which in nature work both aerobically and anaerobically. How many nominally aerobic processes can we list under one of the three subcategories? How about slow sand filters, high-rate trickling filters, low-rate trickling filters, contact beds, Hayes process, activated sludge, extended aeration, Passvier ditches, and a few more? The matrix, for that is what we have, depending on how closely one defines each simple single unit process or unit operation, can extend to nearly 100 possibilities. The combinations and permutations possible for a treatment plant are somewhat horrific to contemplate, especially if operating from a zero based budget. Incidentally, a few people have observed that insofar as research on treatment of refinery wastewaters, we have been operating from a zero base budget for the last eight years, so anything would be an improvement--I didn't say that; I'm just repeating it.

One of the most apparent, logical, rational approaches in winnowing out the more promising treatment options for any given effluent is the good old state-of-the-art approach. Investigate what has been done; compare the results to what is being done; what has been dropped; what appears capable of refinement; and concentrate on the most promising. Admittedly, a state-of-the-art project is highly attractive to many of us bureacrats; after all, it costs relatively little money; it seldom fails to yield a nice thick pile of paper as a report, and it cannot be attacked technically except on the grounds of illiteracy, if the author has failed to research thoroughly all previous references and include them in his document. Rest assured that the state-of-the-art, which initiated research in refinery wastewaters at the Kerr Laboratory was not predicated on this "safety first basis," but the fact that we had very little money, a small staff, and as it appeared from the recommendations of the finished document, a lot to do.

It is generally conceded that it is wise to be aware of the physical, chemical, and biological characteristics of any wastewater which you wish to treat. Since treatment plants involve a sizeable investment of time, money, construction materials, and possible untoward affects downstream (should they fail to perform as designed), a companion report to the state-of-the-art was prepared to delineate wastewater characteristics of the various unit processes and unit operations which existed in a modern refinery, and which, together, represented the composite wastewater stream. Actually, it was not until several years after these two reports were published that we obtained a good statistical basis with respect to only the most common physical and chemical parameters for the composite stream. This basis was developed during the EPA/API Wastewater Characterization Survey which happened to be another Effluent Guidelines Division technical assistance project. The present EPA/API study for the Effluent Guidelines Division will develop similar information with respect to many, but not all, of the organic chemicals and their characteristics in refinery wastewaters. No such study, however, is currently planned with respect to the characteristics of individual unit process or unit operation effluents. Yet, we know that they vary widely, on the basis of singular or limited observations, from one process to another, from one unit operation to another. Since it's generally easier to find the needle in a bale of hay rather than the entire stack, I would commend to your reflection that this is a fertile area for some future research.

From these two cited documents, plus some black magic or legerdemain known as a planning system, we developed an in-house document which laid out on a PERT-type chart our research program in terms of where we had to go and how to get there--a plan for obtaining the most widely usable results for our limited research dollars. Although barred from including air pollution control and solid waste control research, the program document itself did recognize the obvious inter-relationships between the three media and did attempt at all times to prevent creating a new problem in the course of finding a solution to an existing problem. We did this without the usual standing jokes about, "what the hell, let's airstrip it and let the air polluters worry about it." Built into the research program, and continuously upgraded as technology and techniques allowed, was the concept of quality control from initial research project design through the sampling procedures through the analytical procedures to the data evaluation procedures. Those of you who have been associated with projects which EPA has funded are aware of EPA's analytical and quality control manuals--the "CuSum" statistical quality control procedure in the latter manual was developed originally at the Kerr Laboratory.

It is germaine to our forum to review the findings of the original state-of-the-art report and compare them to the projects which have been developed since the start of the program in 1968, nearly one decade ago. Particularly of interest, are those recommendations which were not acted upon through lack of applicant, lack of funding, or lack of analytical and engineering technology. Some are specifically pertinent to the potentially painful problems that we are facing now regarding the "priority pollutants." With your permission I will read these 20 recommendations, instead of depending on memory, because some of them are so beautiful in their simplicity and yet farsightedness:

"1. Develop sampler to obtain representative samples of floating oils, dissolved oils, emulsfied oils, and oily sludges."

Has anyone yet developed a sampler that would do all that? I think not. There has been progress but a representative sample still remains one of the most difficult and probably one of the impossible things to obtain from any wastewater stream.

"2. Conduct internal refinery studies to reduce waste volumes and strengths for old and new refineries."

Back to unit process and unit operation waste streams. Has anyone done any definitive study of these? In a few instances, that I am aware of, yes. We are beginning to approach the area of this recommendation, but not extensively.

"3. Extend biosystem studies to optimize treatment efficiencies and handle shock loading."

Admittedly, there has been a great deal of work on optimizing biosystems from an operational standpoint. A project in an allied field of research may have developed a monitor that, while not eliminating shock loading, will at least give adequate forewarning to divert and hold spills or shock loadings and toxicants that might upset a biological system until they can be handled separately, diluted, or bled back through the system at an acceptable concentration.

"4. Devise a continuous monitor for hydrocarbon detection in wastewaters using common refinery laboratory equipment."

One of our laboratory scientists has developed a procedure using a gas chromatograph, which is now common equipment in most laboratories, to determine hydrocarbons in wastewater. As opposed to the freon, or petroleum ether, or carbon-tetrachloride or hexane or whatever your solvent preference is for oil and grease extraction procedures, this method appears to have repeatability and reproducability characteristics.

"5. Design original wastewater treatment systems for the petroleum industry."

In the case of new grassroots refineries, scarce as they are, this is being accomplished.

"6. Perform chronic (long term) toxicity studies on treated effluents."

Our Laboratory in conjunction with Dr. Mount's Laboratory in Duluth, Minnesota, has started some screening studies in this area. Additionally, some work has been done at Oklahoma State University.

"7. Identification of toxic components in petroleum wastewaters."

Refer to the forum program for further information.

"8. Develop efficient devices and techniques to remove oil spills on diverse waters surfaces (i.e., swamps, rivers, and turbulent seas)."

One of Murphy's laws; if you're going to handle the stuff, pump it, or process it, sooner or later you're going to spill some of it. A great deal of money has been expended in developing spill clean-up equipment, procedures, processes, and techniques. But a total answer approaching a respectable efficiency for all problems of all types of spills is still not within our reach.

"9. Assess environmental effects of spilled oils (i.e., volatile, soluble, emulsified, floating, etc.,) and oil products."

My God, that's many life times of work for many biologists in one simple statement.

"10. Investigate use of cooling towers for treating selected refinery wastewaters for recycling."

How much has been done? Well, some--we're far away from covering all aspects though, nearly a decade later.

"11. Study water reuse within refinery."

Now certainly a good deal has been accomplished in this area. Not all of it in the last 10 years--some of it was done prior to that time--and yet there have been significant accomplishments in the last decade.

"12. Explore feasibility of phenol removal from wastewaters using phenol-soluble oils."

There is more than one plant in the country today that is extracting phenol using solvent extraction processes.

"13. Perform economic studies of brine treatment and disposal on land and sea."

This is still a very sticky problem from the standpoint of what do you do with it regardless of how you manipulate inorganic salts that constitute brine, whether they're from a producing well or a desalter, you still have the salt left over, and you can't burn it, you can't eat it, you can't sell it, you can't use it, and you can't dump it--unless you are lucky enough to be on the coast. Most of the brines approximate seawater; admittedly individual component concentrations range widely, but the components do approximate seawater in terms of numbers and types of elements.

"14. Develop remote sensing techniques for detection of oil and brine pollution."

Supposedly, the CIA can read a license plate from 400 miles out in orbit via satellite, but nothing approaches that degree of precision and accuracy with respect to this simple little recommendation of 10 years ago.

"15. Perform feasibility studies on by-product recovery from refinery wastes."

The phenol recovery technique referred to earlier is, in fact, one of these by-products recovery operations in actual practice.

"16. Devise a monitoring program to prevent subsurface pollution from abandoned oil wells."

There has been a considerable expenditure of EPA funds on a GE project called Tempo having to do with monitoring techniques of groundwater sources and the presence, direction of flow, and source of groundwater pollution. Yet, there remains a great deal to be done to put these into effect with respect to individual plant areas; tank bottoms fail and buried transfer lines will leak.

"17. Examine pollution problems associated with extreme cold in the Alaskan oil fields."

There's one where they really put some money into. Considerably more apparently than any of these other 20 recommendations.

"18. Determine proper measures to collect and reuse waste oils from U.S. vehicular and boat service stations."

This is something that has probably been beaten to death in terms of rerefining of lube oils; nevertheless, from the amount produced each year versus the amount that is used, even in cars that are as smoky as mine there are volumes of lubricating oil that are not reclaimed and not reused--that are dumped in places damaging to the environment.

"19. Design antipollution devices and management controls to insure proper storage of crude oil."

As mentioned earlier, those tank bottoms will fail, transfer lines will leak, and hoses will rupture. I cannot say that there hasn't been a great deal of progress in 10 years in this particular area; but these excursions still occur from time to time with great fanfare and headline publicity usually connected with a tanker loss. Finally, this is the real "catch 22" that will occupy much of your time this week--

"20. Assess toxicological aspects to man and to warm-blooded animals ingesting oil and oily substances."

That was a rather obvious one, wasn't it. Looking back now it's rather obvious to see the wisdom in that recommendation, but we're just now starting to scratch the surface of it in reality. Admittedly, some of these may have been limited by the lack of analytical equipment. Some 20 or 25 years ago, the mass spectrometer was the answer to "on line" process control equipment for refineries, but that didn't work too well. Then the gas liquid chromatograph came along and everybody dumped their mass spectrometers and bought GLC's and hooked them up as process control instruments, and they worked, but not too well. Finally, we have third generation interfaces between the two instruments which we are utilizing to separate and identify these relatively minute traces of organics in treated wastewater effluents.

A few examples of the conclusions in completed extramural reports include:

"Fluid Bed Incineration of Petroleum Refinery Wastes" - American Oil Co.

1. The fluid bed incineration process has been demonstrated to be practical and effective for the disposal of petroleum refinery generated spent caustic and oily sludge.

2. The process creates no atmospheric pollution problems, emitting only carbon dioxide nitrogen and water vapor. The odor of the off gas has been described by various observers as being slight to non-existent.

3. The ash produced contains sodium carbonate, sodium sulfate, other soluble inorganic salts and inert material such as sand, clay, rust, etc.

4. Operations are frequently prematurely terminated by the loss of bed fluidity caused by excessive bed particle size. The particle size growth rate can be controlled by including salient design features and by exercising proper operating techniques.

"Oily Waste Disposal By Soil Cultivation Process" - Shell Oil Co.

1. Disposal of oily sludges (hydrocarbon) by microbial action in cultivated soil has been demonstrated at prevailing soil and climatic conditions at Deer Park, Texas.

2. Three simultaneous experiments with three oils, i.e., crude oil, bunker C fuel oil, and waxy raffinate oil, indicated decomposition rates for the three oils to be approximately equal and averaged about 0.5 pounds of oil per cubic foot per month without adding nitrogen and phosphorus nutrients and about 1.0 pound per cubic foot per month when fertilizers were added. This is equivalent to about 70 barrels of oil per acre per month.

3. Cost of the soil cultivation process based on the demonstration project expenses and a disposal rate of 70 barrels of oil per acre was $7.00 per barrel of oil. Assuming oily sludges and waste materials contain 33 percent oil, the disposal cost by the soil cultivation process would be about $3.00 per barrel.

4. An optimum fertilization program appears to be a) the initial addition of chemicals, if needed based upon soil test results, to attain a slight excess of nitrogen, potassium, and phosphorus, and b) test at regular intervals, once per month, for ammonia and nitrate contents of the soil and add small dosages of ammonium nitrate as needed to maintain a positive test result (10-50 ppm) for ammonium and/or nitrate contents.

5. The major species of microorganisms present are members of the genus Pseudomonas, Flavobacterium, Nocardia, Corynebacterium, and Arthrobacter. The nature of the hydrocarbon substrate did not appear to influence the type of organisms present but did affect the number of bacteria in the soil. Crude oil tank bottoms produced the highest count, waxy raffinate oil produced an intermediate count, while bunker C fuel oil exhibited the lowest microbial population. Temperature appeared to have no effect upon the microbial count and distribution. Addition of fertilizer did not affect the microorganism distribution but appeared to be directly related with the total aerobic count.

6. Oil decomposition rates were low when the concentration of oil in the soil approached the starting condition of 10 percent oil in the soil. Also, the low reaction period coincided with the winter months and low temperature period.

7. Both aromatic and saturated hydrocarbons were reduced with time in the soil for crude oil tank bottoms and bunker C fuel oil. Only the saturate fraction of waxy raffinate oil appeared to be reduced by soil microbial action at conditions existing during the project period.

8. Infrared and gas chromatographic analyses of the oil added to and extracted from soil indicated a) the absence of organic acids in oils added to the soil and the presence of organic acids in each of the extracted oils (oils from plots that were fertilized showed higher concentrations of organic acids), b) the organic acid increase coincided with a decrease in total saturates, and c) the percent weight boiling less than 500°C generally was lower for the oil extracted from the soil at the finish of the project than for either the oil added to or the oil extracted from the soil at the start of the project (the lowest percent weight boiling up to 500°C was extracted from soil which had received the largest quantity of fertilizer materials).

9. Oil and fertilizer chemicals did not infiltrate vertically into the soil at the test location and condition.

10. Rainfall runoff water contained 30 to 100 ppm oil. This oil appeared to be essentially naphthenic acids based upon infrared inspection of oil fractions. Also, rainfall runoff water contained ammonia (nitrogen nutrient) approximately proportional to the excess ammonia content of the soil. Phosphorus and nitrates were not found in runoff water.

11. Oil and nutrient contents of rainfall runoff water from the soil cultivation process can be relatively high, and this discharge water should receive treatment before entering public waterways.

"Refinery Effluent Water Treatment Plant" - Atlantic Richfield

1. Reduction of Chemical Oxygen Demand (COD) content in refinery wastewater effluent has been demonstrated to be feasible by using activated carbon as an adsorbent.

2. The system performed well in that it demonstrated an ability to start up and shut down without delay or difficulty. This gives the process a distinct advantage over biological units for use in handling intermittent rainfall.

3. During the two-year project the unit was operated at an overall average cost of 49 cents per 1000 gallons of water treated or 24 cents per pound of COD removed from the

effluent wastewater. The first year's operational costs were 62 cents per 1000 gallons of water treated, or 34 cents per pound of COD removed. After improvements over the first year's operation, the costs during the second year were reduced to 40 cents per 1000 gallons of water treated, or 18 cents per pound of COD removed.

4. The plant demonstrated excellent reliability.

5. The carbon adsorption plant has demonstrated that when the feed COD is controlled to an average of 233 ppm, the plant can treat refinery water using 8.5 pounds of carbon per 1000 gallons treated and reduce the effluent COD to an average of 48 ppm with a high level of 95 ppm.

"Chemical Coagulation/Mixed-Media Filtration of Aerated Lagoon Effluent" - American Oil Co.

1. Chemical coagulation/mixed-media filtration has been demonstrated to be an effective tertiary water treatment for accomplishing further reductions in suspended solids, oil content and biochemical oxygen demand following a refinery end-of-pipe treatment sequence consisting of an API separator and aerated lagoon.

2. The most significant factors influencing the treatment effectiveness in the scalping mode operation are incident contaminant concentration, the applied chemical treatment level, and seasonal aerated lagoon conditions.

3. Backwashing with lagoon water will keep the filter media satisfactorily free of oil and waste accumulation, and returning the backwash waste to the lagoon can be handled in a way to avoid unmanageable sludge buildup.

4. The filtration facilities require a minimum amount of operator attention and generate no objectionable wastes or odors.

5. The unit operation can be demonstrated easily, appearance of the effluent is greatly improved and the facility therefore has considerable public relations appeal. Both the process and the results are easily visible and comprehensible.

6. Unless adequate hydraulic controls are provided, the filter media can be physically disturbed, rendering it less effective than designed. Safeguards are necessary to prevent such distrubances.

7. Optimized operation to achieve near potable water quality clarity requires response to the required water chemistry for destabilization of colloidal material. This response may

require taking any, or all, of the following into account: 1) pH control; 2) two or three chemical destabilization systems, and 3) reduced hydraulic loading at water temperatures less than 15.5°C (60°F).

8. Brackish water has a major impact on the effectiveness of destabilization chemicals.

9. Brackish water interferes with direct usage of zeta potentials for determining optimal chemical pretreatment because the reduction of zeta potential by double layer repression must be detected. This is readily achieved by determining zeta potentials on diluted samples.

10. Colloid entrapment and double layer repression are destabilization mechanisms to be sorted out and avoided for direct filtration.

11. Charge neutralization and bridging are required destabilization mechanisms for optimal filter performance.

12. Weakly anionic polyelectrolytes are much more effective than nonionics for filter aids in a three chemical system.

13. Even with optimized chemical pretreatment, filter loading must be decreased with decreasing water temperatures.

14. Recommended filter hydraulic loadings are proportional to the viscosity of water.

15. Incorporation of powdered activated carbon up to 150 mg/l had no favorable impact on the destabilization chemistry of biocolloids.

In-house reports and papers produced by program personnel include:

"Analytical Variability of Five Wastewater Parameters - Petroleum Refining Industry" - Petroleum-Organic Chemical Wastes Section, Robert S. Kerr Environmental Research Laboratory.

1. The chemical oxygen demand (COD) test had a repeatability expressed in terms of standard deviation of 9.5 milligrams per liter (mg/l) for petroleum refinery wastewater which had a COD average of 134 mg/l. Reproducibility for this same refinery wastewater exhibited a standard deviation of 15.0 mg/l.

2. Suspended solids with an average concentration of 19 mg/l had a standard deviation for repeatability of 1.8 mg/l and a standard deviation for reproducibility of 5.2 mg/l.

3. Results obtained for the ammonia test with an average concentration of 8.5 mg/l exhibited a repeatability standard deviation of 0.1 mg/l and a reproducibility standard deviation of 0.9 mg/l.

4. The repeatability standard deviation for phenolics was 0.2 mg/l for a sample containing 5.5 mg/l; the standard deviation for reproducibility of phenolics was 0.8 mg/l.

5. Oil and grease standard deviation for repeatability was 2.3 mg/l and reproducibility was 2.9 mg/l for a sample containing approximately 11 mg/l.

6. There does not appear to be any major differences in concentration between the results of hexane extraction and freon extraction procedures.

7. The variance of the analysis for oil and grease appears to be less for the freon method than the hexane method.

8. A better than 95 percent spike recovery for COD and ammonia was achieved.

9. A comparison of results between Phases I and II indicate the instruction seminar, which was held to achieve uniformity of analytical procedures accomplished:

   a. A significant reduction in arithmetic and extreme outlier value errors;

   b. Enhancement of uniformity of laboratory technique;

   c. Minimizing the COD mean values between intralaboratory and interlaboratory results;

   d. Improvement of spike recovery for COD and ammonia.

10. The standard deviations for COD, ammonia, and phenolics were decreased between Phase I and Phase II.

11. Environmental Protection Agency (EPA) methodology for the parameters studied appeared applicable for petroleum refinery wastewater when the analysts were properly instructed.

"Acute Toxic Effects of Petroleum Refinery Wastewaters on Redear Sunfish" - John E. Matthews and Leon H. Myers, Robert S. Kerr Environmental Research Laboratory.

1. Short-term static bioassays of 24-hours' duration can be an effective tool for screening industrial process wastewaters to locate sources of toxic agents; these tests can also be used to evaluate effectiveness of industrial waste treatment processes.

2. Static bioassays cannot be used to obtain reliable 50 percent tolerance limit (TL_{50}) values for low toxicity wastes that exert a high oxygen demand although a range can often be established by an experienced observer. Dissolved oxygen (DO) usually becomes critical at about 12 hours; low DO plays a maor role in a mortaility after this time. Activated sludge treatment processes tend to reduce the oxygen demand beyond the critical stage.

3. Raw wastewaters from different oil refineries vary greatly in their toxic characteristics; wastewaters from different processes within a single refinery also vary greatly in their toxic characteristics. Toxicity of oil refinery wastewaters varies considerably at different treatment stages in the activated sludge process; toxicity appears to decrease following each stage of treatment.

4. Toxicity of oil refinery wastewaters cannot always be predicted from results of chemical analyses; the toxic effect of the waste is dependent on the synergistic or antagonistic activity of toxicants present.

5. The most common toxic constituents of untreated oil refinery wastewaters are: ammonia, sulfides, phenolic compounds, and cyanides. Raw wastewaters also may contain other toxic compounds including various hydrocarbons.

6. Due to the volatile and unstable nature of some toxic components of oil refinery wastewaters which may have led to a reduction in concentrations during sample transportation, storage, andhandling, TL_{50} values obtained during these tests may be higher than the actual value.

7. Acute toxic effects of raw wastewaters from oil refineries are generally exerted within the first 12 hours of the static test; therefore, a 24-hour test will provide good positive results under static conditions. If samples containing toxic compounds, other than those mentioned above, toxic effects may be exerted over an extended period. Tests should then be continued for at least 48 hours to obtain more positive results.

8. Toxicity of the final clarifier effluent from oil refineries with activated sludge treatment systems is dependent on toxic constituents present in the influent and their concentrations. Results of chemical analyses conducted during these tests indicate that concentrations of most toxicants other than ammonia are reduced by activated sludge treatment systems and at least a four-fold decrease in toxicity can be expected after treatment.

9. Although activated sludge treatment systems have very little effect on ammonia concentrations, the toxic effect of ammonia is lessened due to a decrease in pH of the treated effluent.

A listing of some of the current funded research may be of interest:

"Identification of Refractory Organic Compounds from Treated Refinery Wastewaters" - ERDA, Division of Environment & Safety, Washington, D.C. Project Site - Argonne, Illinois

"Cyanide Removal from Petroleum Refineries" - Illinois Institute of Technology Research Institute, Chicago, Illinois.

"Refinery Sour Water Stripper Studies" - American Petroleum Institute, Washington, D.C. Project Site - Ponca City, Oklahoma.

"Powdered Carbon-Activated Sludge-Filtration Processes for Petroleum Refinery Wastewater" - Atlantic Richfield Co., Harvey, Illinois.

In closing, the lesson which I hope we have learned from this recapitulation of the Laboratory's research program history is that the list of priority pollutants will not be an end in itself. We should apply the available technology to its utmost to determine what is in an effluent, where it came from, and how to remove or control it, if it is present in environmentally significant amounts. Such approach may avoid or at least ameliorate future crises.

Despite having disposed of soothsayers earlier, the urge to predict is too strong to resist. Try these with respect to the priority pollutants list.

1. Some compounds on the list ain't gonna be found in refining effluents

2. Some compounds not on the list will be found in refining effluents

3. If you continue to search long enough and hard enough for something you may find it anywhere--even though it ain't really there. Now ponder on that one a while.

DISCUSSION

Paul Mikolaj, Lion Oil Company: Is there any research work being done on radiation techniques to treat wastewater?

Marvin Wood: There is, of course, some being done, but none that I am aware of or at least none that we are funding in this specific area of refinery wastes. There is some being done in the case of other wastes--domestic and possibly a few cases of industrial. It might involve come coblat 60 or something sources or radiation to change the physical characteristics to make the wastes more amendable to handling.

BIOGRAPHY

Marvin L. Wood holds a B.S. in Chemical Engineering from the University of Arkansas and an M.S. in Instrumental Science from the Graduate Institute of Technology of the University of Arkansas at Little Rock. He is currently Deputy Director and Chief of the Source Management Branch of the EPA's Robert S. Kerr Environmental Research Laboratory at Ada, Oklahoma.

SESSION II

"PANEL DISCUSSION: RESEARCH SUPPORTED IN THE PRIVATE SECTOR"

Chairman

*Milton R. Beychok

Consulting Engineer
Irvine, California

Panel Members

Robert T. Denbo
Exxon
Baton Rouge, Louisiana

Kent G. Drummond
Marathon Oil Company
Findlay, Ohio

Francis S. Manning
University of Tulsa
Tulsa, Oklahoma

David C. Bomberger
Stanford Research Institute
Menlo Park, California

Judith G. Thatcher
API/DEA
Washington, D.C.

*Biography on Page 300

"DISCUSSION OF RESEARCH RELATED TO PETROLEUM REFINERY WASTEWATER SPONSORED BY THE API COMMITTEE ON REFINERY ENVIRONMENTAL CONTROL"

Robert T. Denbo
Coordinator of Environmental Control, Exxon
Baton Rouge Refinery

Mr. Drummond's and Ms. Thatcher's papers discussed the organization of the Division of Environmental Affairs of the American Petroleum Institute and research sponsored by the Division of Environmental Affairs. This paper will cover the research program sponsored by the Committee on Refinery Environmental Control (CREC).

First, some added background on the API. The API was incorporated in 1919. The objectives were set forth as follows:

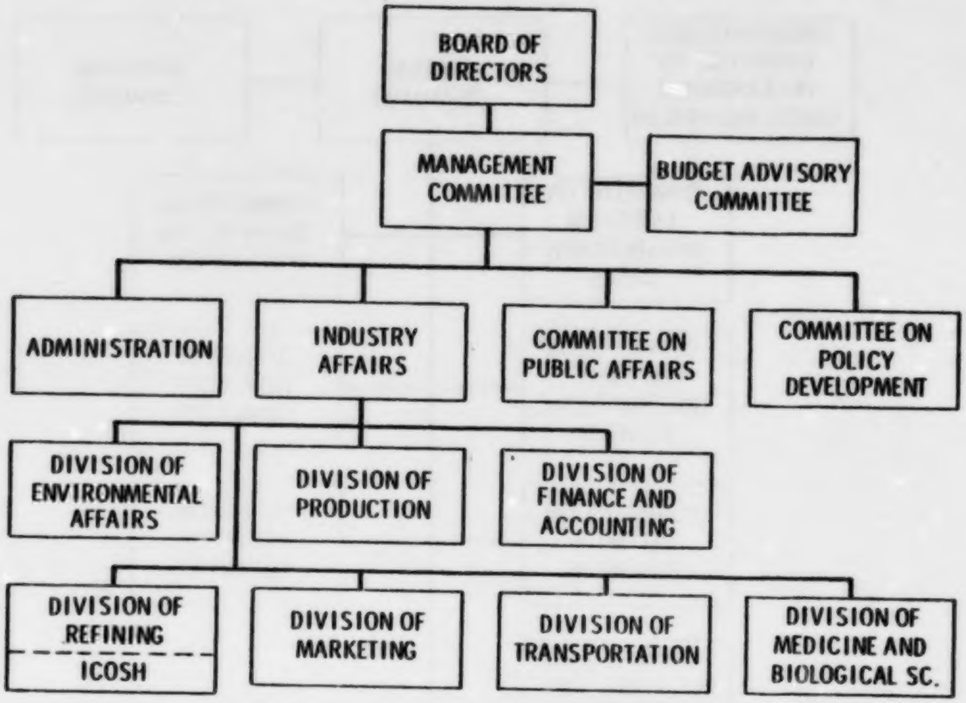
- afford a means of cooperation with the government in all matters of national concern.
- foster foreign and domestic trade in American petroleum products.
- promote, in general, the interest of the petroleum industry in all its branches.
- promote the mutual improvement of the members and the study of the arts and sciences connected with the petroleum industry.

Next, it may be appropriate to put the CREC Committee in proper prospective in the American Petroleum Institute. The first chart shows the organizational setup in API down to the divisional level.

The second chart shows the relationship of the CREC Committee to the General Committee of the Division of Refining. The CREC Committee was set up to have the following responsibilities:

- the development and publication of the API Manual on Disposal of Refinery Wastes which covers atmospheric emissions, solid wastes and liquid wastes.
- the sponsorship of research related to refinery pollution control.

AMERICAN PETROLEUM INSTITUTE


BOARD OF DIRECTORS
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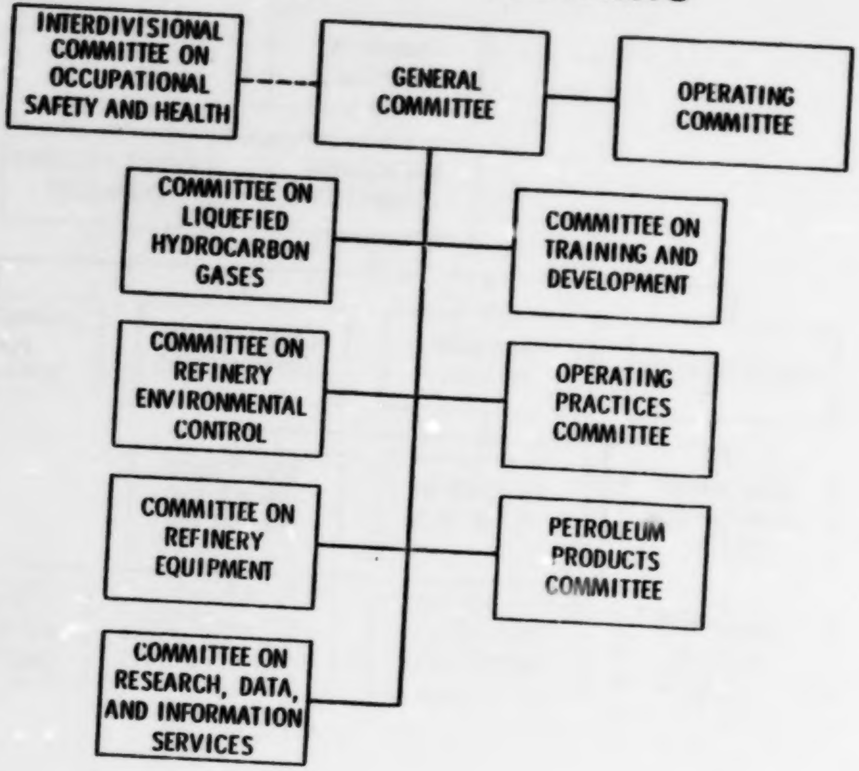
ADMINISTRATION
INDUSTRY AFFAIRS
COMMITTEE ON PUBLIC AFFAIRS
COMMITTEE ON POLICY DEVELOPMENT
DIVISION OF ENVIRONMENTAL AFFAIRS
DIVISION OF PRODUCTION
DIVISION OF FINANCE AND ACCOUNTING
DIVISION OF REFINING
ICOSH
DIVISION OF MARKETING
DIVISION OF TRANSPORTATION
DIVISION OF MEDICINE AND BIOLOGICAL SC.

DIVISION OF REFINING


INTERDIVISIONAL COMMITTEE ON OCCUPATIONAL SAFETY AND HEALTH
GENERAL COMMITTEE
OPERATING COMMITTEE
COMMITTEE ON LIQUEFIED HYDROCARBON GASES
COMMITTEE ON TRAINING AND DEVELOPMENT
COMMITTEE ON REFINERY ENVIRONMENTAL CONTROL
OPERATING PRACTICES COMMITTEE
COMMITTEE ON REFINERY EQUIPMENT
PETROLEUM PRODUCTS COMMITTEE
COMMITTEE ON RESEARCH, DATA, AND INFORMATION SERVICES

- the dissemination of information on legislative developments concerning stream and air pollution and solid waste disposal.

It is within this context that the R&D related to petroleum refinery wastewater is carried out. During the past few years, CREC has worked closely with the API Division of Environmental Affairs and participated actively in many of the projects of the Water Quality Committee. CREC's own research and development and related studies have resulted in the publication of the following reports:

- the volumes on liquid wastes including:
  - o separator design parameters
  - o biotreatment design parameters
  - o stripping
  - o extraction
  - o adsorption
  - o and other areas

- a filtration volume

- a sour water stripper volume.

The following projects are currently in the planning stage tentatively for 1978:

- Enhancement of biological treatment - Phase III

- Studies of handling of storm runoff from petroleum refineries

- Studies of variability of treated effluents

- Benthic assays of treated refinery effluents.

The following two projects will be discussed briefly in this paper for purposes of illustration, how research and related studies are developed in the CREC Committee:

- Sour water stripping

- Bioenhancement

Sour Water Stripping

Sour or foul water in petroleum refining is process water containing organics that also contains more hydrogen sulfide and ammonia than can be handled effectively in a biological treatment system. The types of organics present in this stream include phenolic type compounds and other objectionable materials. This type of water is probably the most difficult to handle of all process waste waters in most refineries. It is usually produced in such operations as a steam condensate from catalytic cracking, coking, hydrocracking and other hydroprocessing. Effective removal of the hydrogen sulfide and ammonia are essential to allow meeting limits on these two compounds and to permit effective biological oxidation of the phenols and other organics.

Ron Gantz of Continental Oil has been the guiding hand in the CREC-sponsored studies by contractors to improve the efficiency of removal of these two constituents by steam stripping which is the existing state of the art. The current program of study has extended over a period of more than three years and has been, in part, a joint effort by EPA and API CREC. The EPA Water Labs at Ada, represented by Leon Myers, played a significant role in the development of this work. The program has consisted of extensive surveys of actual plant operations to determine state of the art in the industry, plant testing to obtain actual operational data, the operation of pilot facilities in laboratories, and the correlation of all the results into a comprehensive, new equilibria calculation procedure.

The results from these studies are to be published soon. The most significant findings include:

- the identification of ammonia that cannot be removed by stripping from the water as produced - so called "fixed ammonia". This fixed ammonia apparently will not come out of solution by stripping if it exists as ionic ammonia in combination with carboxylic acids and other such compounds when slightly acidic. It was found that the presence of a slight excess of sodium hydroxide over the stoichiometric amount will allow stripping to proceed efficiently.

- another significant result has been the development of a new equilibria calculation procedure. New equations have been developed and tested which give much more accurate results and can be used more flexibly than existing accepted approaches. The procedure exists as a computer program which will permit calculations including the effect of pH adjustments at selected points in the stripper tower. This is not possible in the existing sour water stripping computational approach.

Bioenhancement

The CREC study of bioenhancement will be covered in some detail in Session VIII of this open forum by Lyn Crame of Texaco. Consequently, it is not appropriate to go into the findings of this study in this paper.

However, it is pertinent to say that this study was started about a year ago prior to the availability of initial results from other API studies which were designed to determine the presence of residual organic compounds in refinery effluents after biological treatment. By "residuals" is meant organics present in the effluent which were introduced in the raw waste load feed to biological treatment. Initial results of the study indicate only a small amount of residuals are present in biologically treated effluent. Apparently the vast majority of organics in the treated effluent are metabolities, humic acids, and other compounds associated with the biodegradation process. Almost no objectionable compounds have been found in biologically treated effluents. At this point it would not appear that it is practical to require further treatment on the basis of results of conventional analyses or even results on the basis of analyses for the more exotic list of toxic compounds.

Conclusion

The CREC program for the past few years has been consistent with the topics discussed at this open forum. The agenda of this open forum suggests the high degree of sophistication that is employed in the treatment of refinery wastewater. It can also be said that the performance of treatment facilities for petroleum refineries suggest that the current quality of treated wastewater from these refineries is no longer a significant problem in water pollution abatement. It appears that technology and research in this area has advanced to the point where it is well ahead of other areas of environmental concern for the industry.

BIOGRAPHY Robert T. Denbo

Robert T. (Bob) Denbo is the coordinator of environmental control at Exxon's Baton Rouge Refinery. In this capacity, he is responsible for development of long-range goals for air and water conservation and solid waste disposal problems.

Mr. Denbo received a B.S. degree in Chemistry from Louisiana State University in 1948, finishing the work for his degree after spending four years in military service during World War II. Mr. Denbo has been with Exxon in Baton Rouge since 1948.

He is currently chairman of an Exxon committee concerned with environmental control for all domestic refineries. He is chairman of the American Petroleum Institute Committee on Refinery Environmental Control, member of the API Division of Environmental Affairs, former president of the Louisiana Water Pollution Control Association, member of the Technical Advisory Committee to the Louisiana Air Control Commission, and member of the Air Pollution Control Association. Mr. Denbo has served on a number of panels related to development of information on target values for U. S. refinery water effluents. He has served on a joint U. S.-Soviet planning group for cooperative effort in refinery water pollution controls.

WATER QUALITY COMMITTEE OF API

Kent G. Drummond
Technical Coordinator, Environmental Control Div.,
Marathon Oil Company

The Water Quality Committee is one of eight standing technical committees under the General Committee on Environmental Affairs (see Figure 1). The General Committee is composed of 28 oil company environmental coordinators. Under the General Committee are 8 standing committees which have over 50 task forces involving more than 300 oil company personnel.

These committees meet on a regularly scheduled basis of twice a year; once in the spring to review current projects and to generate new projects for the forthcoming year and again in the fall to review current projects. The spring meeting is the normal time for proposing the next year's budget.

In the case of the Water Quality Committee, if a project is accepted by our committee, it is then proposed as part of the committee's budget, to the Planning Budget Advisory Committee which is under the General Committee on Environmental Affairs. Incidentally, each standing technical committee has a liaison representative from the Planning Budget Advisory Committee.

If PBAC approves the project, it is then submitted to the parent Environmental Affairs Committee for consideration. The project then becomes part of the proposed budget of the Environmental Affairs Committee to be considered by the API Finance Committee and, if approved, becomes a funded project for the new year's budget.

Figure 2 lists the members' company affiliation on the Water Quality Committee. Of the 18 members on the Committee, only 2 companies have 2 representatives and this is because their respective representatives are either chairmen of more than one task force or are a representative from the Committee on Refinery Environmental Control.

There are 3 main project areas of interest as shown in Table 1. The Water Quality Committee is primarily interested in the quality of water as it leaves the premises. We also become involved in projects which need immediate attention. At other times, we get into projects which are beyond the monitary scope of the various divisions.

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Later on this afternoon, Mrs. Judith Thatcher will discuss 2 of the projects which come under the Water Quality Committee.

In 1977, we had 10 active projects. These projects are listed in Table 2. Their names and the budgetary allocations are given. Our original budget of $240,000 was approved in December, 1976, however, because of the changes in government regulations, we came back with the supplementary budget of $450,000 in March, 1977. Project W-14 and the last 4 items on Table 2 were approved at that time.

Our 1978 proposed budget came to a total of $515,000. This is shown in Table 3.

For the past five years, the budgetary allocations for the Water Quality Committee have continued to grow. Back in 1974, we had a budget of only $60,000; whereas in 1978, our proposed budget is $515,000 plus 40% of $450,000 which is $180,000; making a total of $695,000 for the year of 1978. This is all shown on Figure 3.

In the past six years, the Water Quality Committee has attempted to learn more about our own refinery operations. With this better understanding, we have been able to defned ourselves against unreasonable regulations and to discuss with EPA regulations which we feel attainable.

The five projects which we have proposed for 1978 will help us to better understand some of the problems within our refineries and hopefully, this will lead to guidelines in 1983 which are attainable and will give best valuable treatment economically achievable.

BIOGRAPHY Kent G. Drummond

Kent G. Drummond is Technical Coordinator in the Environmental Control Division of Marathon Oil Company, Findlay, Ohio. He has a B.S. degree in Civil Engineering and a M.S. degree in Sanitary Engineering from Iowa State University. He is currently Chairman of API's Water Quality Committee and Chairman of the 1979 Oil Spills Conference.

TABLE 1

WATER QUALITY COMMITTEE PROJECT AREAS OF INTEREST

1. Quality of water leaving premises
2. Projects which need immediate attention
3. Projects beyond monetary scope of divisions

TABLE 2

WATER QUALITY COMMITTEE 1977 PROJECTS

No.	Title	Budget $k
W-12	Bioassays of Refining Effluents	$ 90k
W-14	Toxic Pollutant Effluent Standards	$ 25k*
W-15	BPT Vs BAT Petroleum Refining Guidelines	$100k
W-19	Non-process Effluent Standards	
W-20	Analysis of Refinery Effluents (BPCTCA)	$ 50k
W-21	Amendments to 92-500	
W-22	Sampling & Testing Protocol for Toxic Pollutants	$200k*
W-23	Refinery Questionnaire (EPA) Analysis	$100k*
W-24	Refinery Effluent Pollution Contribution in Perspective	$100k*
W-25	Economic Study BPT to BAT	$ 25k*
	Total	$240k $450k*

*Approved March '77

TABLE 3

WATER QUALITY COMMITTEE 1978 PROPOSED BUDGET

No.	Title	Budget
W-12P (cont'd)	Bioassays on Refinery Effluents	$ 40k
W-22P (cont'd)	Sampling & Testing Protocol for Toxic Pollutants	$200k
W-23P (cont'd)	Refinery Questionnaire Follow up	$100k
*W-26P (new)	Removal of Toxics from Refinery Effluents - Pilot Plant (Joint Study)	$ 75k
*W-27P (new)	Evaluation of Selected Hazardous Refinery Chemicals to F.W. Organisms	$100k
	Total	$515k

*Projects to be carried out if significant quantities are found in effluents.

COMMITTEE ON ENVIRONMENTAL AFFAIRS

PBAC

GOVERNMENT LIAISON

COMMITTEES

1. Fate & Effects of Oil
2. Oilspill Prevention & Control
3. Mobile Source Emissions
4. Environmental Economics
5. Stationary Source Emissions
6. Solid Waste Management
7. Air Quality
8. Water Quality

ENVIRONMENTAL AFFAIRS ORGANIZATION CHART
API Environmental Affairs

Figure 1

WATER QUALITY COMMITTEE MEMBERSHIP BY COMPANY

Chairman - Marathon

Vice Chairman - Standard of Indiana

Members

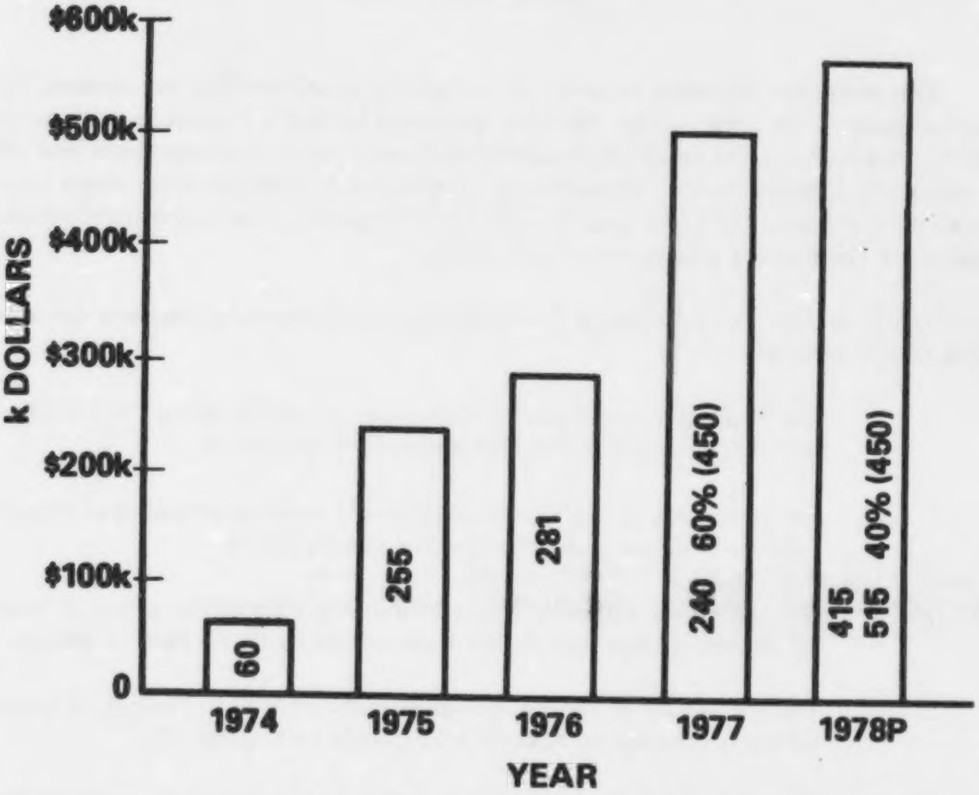
Chairman of CREC - Exxon Refining

Chairman of Liquid Wastes - Union Oil

Task Force Chairman
1. Exxon Research & Engineering
2. Union Oil Co.
3. Gulf Oil Co.
4. Standard Oil of Ohio
5. Shell Oil Co.
6. Shell Oil Co.
7. Sun Oil Co.
8. Mobil Oil Co.

Others
1. Atlantic Richfield Co.
2. Getty Oil Co.
3. Texaco, Inc.
4. Chevron Oil Co.
5. API Representative

Figure 2



WATER QUALITY COMMITTEE PAST BUDGETS 1974 – 1978P

Figure 3

OVERVIEW OF RESEARCH ON PETROLEUM REFINERY WASTE WATERS AT U.S. UNIVERSITIES

Francis S. Manning
Professor of Chemical Engineering
University of Tulsa

This overview addresses research at United States universities not covered by the previous papers. In other words, research sponsored by federal agencies such as the E.P.A.; the A.P.I.; and research institutes has been summarized elsewhere and will not be repeated. Obviously it is impossible to canvas every potential department in every university and hence the following list will be incomplete. The author apologizes to those researchers whose efforts have been omitted.

This overview will not discuss the following studies because they are described elsewhere in this symposium: -

- the Brigham Young study of liquid-vapor equilibrium of H_2S-NH_3-CO_2 which is reviewed by Milton Beychok in Session VI
- the University of California at Berkeley work on stripping of organics using volatile solvents - see Marvin Wood in Session I
- the University of Texas at Austin investigation of the effect of temperature on critical sludge age as this is described by Davis Ford in Session V
- the University of Delaware experiments on PAC in biological treatment which is covered by Francis Robertaccio in Session VII.

This survey uncovered three long-term research programs which, surprisingly, have many common features. All three are sponsored by groups of petroleum and petroleum related industries and all three address very specific research objectives. These three programs at Louisiana State University, Oklahoma State University, and the University of Tulsa are now described.

LOUISIANA STATE UNIVERSITY

The Petroleum Refiners Environmental Council of Louisiana (PRECOL) group has a long history of financial support for environmental research in the Zoology and Physiology

Department at LSU. Initial support occurred in 1946 when the Louisiana Petroleum Refiners Waste Control Council provided two fellowships for the determination of immediate and accumulative toxicity of refinery wastes to fish. Participating companies included Chalmette Petroleum Corporation, Cities Service, Continental Oil Company, Pan American Petroleum Corporation, Shell and Standard Oil.

Bioassay techniques were developed in the 1950's and pesticide toxicity work became the focal point of the laboratory during the 1960's. Emphasis shifted to toxicity studies on the effects of crude oil, emulsifying agents and interactions between them on aquatic fauna during the early 1970's. The organizational name was changed to PRECOL in 1973. The community structure of the Calcasieu estuary began in 1974 along with an investigation of heavy metal movement through the estuary. Two new projects were initiated in 1977. L.S.U. is investigating the accumulation of heavy metals and organic pollutants by water snakes and benthic invertebrates from the Mississippi River near the Baton Rouge industrial complex. The effects of low oxygen tension on the survival and metabolic rate adjustments of aquatic fauna are also being investigated.

Financial support for research efforts has continuously grown as has the number of oil companies providing it. The PRECOL group now consists of: Cities Service Oil Company, Continental Oil Company, Exxon Company, Gulf Oil Company, Murphy Oil Corporation, Shell Oil Company, Tenneco Oil Company and Texaco, Inc. The L.S.U. laboratory has always enjoyed a close working relationship with the Louisiana Division of Water Pollution Control which provides technical support for graduate students.

OKLAHOMA STATE UNIVERSITY

Since 1956 the Oil Refiners Waste Control Council of Oklahoma has sponsored biological investigations on petroleum refinery waste waters in Oklahoma. This work, originally directed by Professor Troy Dorris and directed since 1970 by Professor S. L. Burks, is currently studying:

- The Effects of Residual Volatile Toxins in Oil Refinery Waste Waters
- The Biological Evaluation of BPTCT and BATCT for Refinery Waste Waters
- The Development of Benthic Bioassay Techniques.

At present the Oil Refiners Waste Control Council of Oklahoma includes the following members: APCO, Champlin, Conoco, Hudson Oil Company, Kerr-McGee, OKC Refining Company, Sun Oil, Texaco and Vickers.

The recent biological evaluation of activated sludge, sequential activated sludge-dual media filtration (equivalent to Best Practicable Treatment Control Technology, BPTCT) and sequential activated sludge-dual media filtration-activated carbon adsorption (equivalent to Best Available Treatment Control Technology) at the ETU refinery showed that;

1. Activated sludge and BPTCT would not produce a non-toxic effluent.

2. BATCT produced an effluent which did not cause any significant deleterious effects upon fish, benthic macroinvertebrates, and periphyton during 32-day exposures.

Chemical analyses of the treatment effluent streams indicated that most of the toxicity was associated with the organic substances as measured by TOC and COD analyses.

A new bioassay method for determining the effects of environmental contaminants on populations of benthic macroinvertebrates has been developed. Colonized Hester-Dendy samplers were transported from a natural stream to artificial streams and exposed to industrial waste water. Species diversity, number of taxa, and density of the aquatic organisms were measured before and after selected time intervals of exposure. A 30 and a 32-day continuous-flow exposure test with the benthic macroinvertebrates showed that activated sludge treated petroleum refinery wastewater caused a greater decrease in species diversity than the sequential activated sludge-dual media-activated carbon treated effluent. The effect upon number of taxa and mean density of individuals was even greater. This procedure has permitted exposure of several species of aquatic invertebrates to the test solution and thus measured the effect upon pollution sensitive and tolerant organisms.

UNIVERSITY OF TULSA

The University of Tulsa Environmental Protection Project (UTEPP) began January 1, 1974. The UTEPP program, which is directed by Professor Nicholas D. Sylvester of Chemical Engineering, has received support from the following companies: Ameron, Amoco Production Company, Aramco, Bechtel Corporation, Calgon Corporation, Chevron Research Company, Crest Engineering, Compagnie Francaise des Petroles, Dow Chemical, U.S.A., Exxon Production Research Company, Foster Wheeler Corporation, Getty Oil Company, Iranian Oil Services, Ltd., Lummus Company, Marathon Oil Company, Mobil Research and Development Corporation, and Pullman Kellogg.

Currently the program includes the following projects:

1. Chromate Removal From Cooling Tower Blowdown
   Commercially available ion exchange resins for chromate removal from cooling tower blowdown are being evaluated. The effectiveness of chromate removal, the regenerability of the resins and chromate recovery are being studied.

2. Oil Removal From Wastewaters by Induced Air Flotation
   The effects of oil type, concentration, drop size and size distribution; process residence time, air flowrate, bubble size; and polyelectrolytes on the performance of induced air flotation is being studied.

3. Oil Removal From Wastewaters by Ultrafiltration

The removal of gulf coast crude oil from wastewaters by ultrafiltration is being investigated. The effects of oil type and concentration, flowrate and salt concentration on oil removal efficiency are being studied.

4. Pollutant Removal by Adsorption and Reaction in Aqueous Slurries of Powdered Activated Carbon

The adsorption and oxidation reaction characteristics of pollutants (SO_2 and organics; e.g., benzene) in aqueous slurries of high surface area powdered activated carbon is being studied. In conjunction, the effects of the mass transport processes attendant to slurry reactors on adsorption and oxidation are being determined. In addition, the catalytic activity and mechanisms of activated carbon towards oxidative pollutant removal will be elucidated.

5. Urea Removal From Industrial Wastewaters

A state-of-the-art review of urea removal from industrial wastewaters is being prepared. Although urea is synthesized on a large scale for use in the manufacture of urea-formaldehyde resins, the primary emphasis of the review will be to its manufacture for use as a fertilizer.

6. Activated Sludge Enhancement With Powdered Activated Carbon

An experimental study is being initiated to investigate the mechanisms involved in activated sludge enhancement with powdered activated carbon. In particular, answers will be sought to questions such as:

(i) How much does the blocking of the carbon surface bacteria and their by-products reduce the adsorptive capacity of the carbon?

(ii) What is the mechanism of carbon surface renewal by the action of microorganisms?

In addition, appropriate mathematical models of the process will be developed.

SUMMARY

It is hoped that more universities will become involved in the treatment of refinery wastewaters. While considerable progress has been made due to encouragement and financial support from the U.S. EPA, API, etc., several questions remain to be answered. Some key topics are: -

- the effect of temperature on biological degradation operating performance during the severe winter of 1976-77 has questioned the accuracy of the traditional Streeter-Phelps equation
- the effect of PAC on nitrification
- identifying inhibitors of biological kinetics

- dewatering sludges especially when the contributions from refinery API, DAF, and ASP units are combined.

ACKNOWLEDGEMENTS

Professors Bud Burks; Bill Stickle and Nick Sylvester provided the descriptions of the major programs at O.S.U., L.S.U. and T.U. respectively.

BIOGRAPHY

Francis S. Manning is the Director of the Petroleum Energy Research Institute (PERI) and Professor of Chemical Engineering at the University of Tulsa. He holds the following degrees in Chemical Engineering: - B. Eng. (Hons) from McGill University and M.S.E., A.M., and Ph.D. from Princeton University. He is a professional engineer, registered in Oklahoma, Pennsylvania and Texas. Frank taught at Carnegie-Mellon University for 9 years before joining the University of Tulsa in 1968. The author of one book and over 60 papers, Frank's current research interests lie in thermodynamics, reaction kinetics and industrial pollution control. In 1969 he received the R. W. Hunt Silver Medal from the AIME.

OVERVIEW OF RESEARCH ON PETROLEUM REFINING WASTEWATERS AT INDEPENDENT CONTRACT RESEARCH ORGANIZATIONS

David C. Bomberger
Chemical Engineer, Environmental Control Group
SRI International

The major contract research organizations in the United States were surveyed to determine what research is being done on the wastewaters from petroleum refineries. Companies that were engaged primarily in engineering and design were not contacted. Any research relating to identification of priority pollutants identified in the 1976 Consent Decree is not reported here because it will be covered by other panelists.

Very little research relating directly to refinery wastewater is being done at contract research organizations. Only ten ongoing or recently completed projects were identified, and only four of these were concerned directly with refinery wastewater. The other six projects covered aspects of synthetic fuel production and utility water usage. The results of these projects could be utilized by petroleum refiners through technology transfer.

Most of the research funding is from government agencies, principally ERDA and EPA. Only two projects were funded by private industry, one by a single company and the other by the American Petroleum Institute.

The ten research projects cover four general topics: the cost of effluent treatment, wastewater treatment technology, measurement of wastewater components, and reduction of effluent volume, as summarized below.

Cost of effluent treatment:

- Battelle has studied the economic impact of environmental regulations on the petroleum industry, for the American Petroleum Institute.

Treatment technology:

- SRI International has studied ammonia fixation in sour water strippers, for the American Petroleum Institute (EPA grant).
- Midwest Research Institute has examined a petroleum refinery treatment system, for a refinery.
- Gulf South Research Institute is studying the technology for removal and destruction of organic compounds from wastewater, for the EPA, the State of Mississippi, and private industry.

Measurement of wastewater components:

- Radian is conducting two projects on the development of sampling technology and on analysis of effluents from synthetic fuel production, for ERDA.
- Battelle Northwest is studying the wastewater produced in shale oil retorting, for ERDA.
- Radian is studying fugitive hydrocarbon emissions from petroleum refining, for the EPA.

Reduction in effluent volume:

- Radian is investigating optimization of water use in the utility industry, for the EPA.
- Radian is also studying saline water use in energy facilities, for ERDA.

These last two projects are applicable only indirectly and would rerequire technology transfer.

BIOGRAPHY

David C. Bomberger is a chemical engineer in the Environmental Control Group at SRI International. He has a Ph.D. in chemical engineering from Princeton University. Before joing SRI International, he worked on environmentally related projects for Bechtel Corporation and The Shell Development Company.

"CURRENT API STUDIES OF RESIDUALS IN REFINERY EFFLUENTS"

Judith G. Thatcher
Environmental Associate, American Petroleum Institute

Good afternoon, ladies and gentlemen.

Mr. Drummond has described the general structure of API's Environmental Affairs Department and the type of research carried out under the Water Quality Committee. I would like to discuss two current projects relating specifically to one of the major issues being discussed at this forum, that is, toxic pollutants.

In late 1974, a widely publicized study focused national attention on the presence of a number of allegedly toxic organic compounds in New Orleans' public drinking water. Although the validity of the studies attempting to relate New Orleans' drinking water to disease has been questioned, the studies understandably generated much publicity and public concern. There are many possible sources of organics in public water intakes, including effluents from industrial, chemical, and municipal sewage plants, in addition to surface run-off.

Although much was known in 1974 about refinery effluents with respect to conventional waste water parameters such as BOD and COD, little was known of the nature of the organic residuals contributing to the concentration of these parameters in the final discharge of treated refinery effluents. In order to begin to fill this data gap, funds were made available to begin work in this area. The project was entitled "Analysis of Residuals in Refinery Effluents" and is under the direction of API staff and the W-20 Task Force.

The objective of the first phase of the work was to determine the types and amounts of residuals in the effluent from a refinery meeting BPCTCA, and the potential effects of these residuals on public drinking waters. During Phase I, samples of the intake water and the effluent water from a Class B refinery were obtained, along with samples of the effluent from a municipal sewage treatment plant. It was felt that obtaining and analyzing samples from the treatment plant would lend some perspective in evaluating any residuals found in the refinery effluent. The types of analyses that were run on the samples were metals, polynuclear aromatics, organo-halides and volatile and nonvolatile hydrocarbons. In addition, classical parameters such as COD, BOD, and total suspended solids were run. In order to determine whether any precursors of organo-halides were present in the refinery effluent and intake waters, portions of the refinery intake and effluent samples were chlorinated and then analyzed. The analyses of these samples were then compared to the chlorinated municipal plant samples.

The objective of Phase II is to determine the types and amounts of residuals in a second BPCTCA refinery, and the removal of these residuals across various pilot plant treatment trains. Samples from a second Class B refinery were taken as well as samples from another municipal treatment plant. The Class B refinery is the same refinery sampled for the EPA-Argonne study. This study will be discussed in detail on Thursday by Mr. Fred Pfeffer of EPA's R.S. Kerr Laboratory. In this study, a pilot unit mixed media filter and activated carbon column were set up at the refinery to treat a slip-stream from the refinery activated sludge unit. Samples of the refinery's intake water, DAF and ASU effluents were taken, along with samples of the two pilot units, over a four-day period. API took samples along with EPA at the same time and place. Our analyses were primarily for polynuclear aromatics and organo-halides, whereas EPA determined trace organics present in the samples using gc-ms techniques.

During the planning of the Phase II study, the task force became aware of a pilot study that was to be carried out by Texaco under contract to API's Refining Department. This study consisted of evaluating the performance of several different pilot scale treatment trains -- including powered and granular activated carbon -- on refinery wastewater. The W-20 Task Force decided to take samples across the various treatment trains and analyze them for the presence of polynuclear aromatics and organo-halides. Conventional parameters were measured by Texaco. Details of this study will be given later in the program by Mr. Len Crame of Texaco, Inc.

About the time the scope of the Phase II study was being finalized, the toxics settlement agreement was signed by EPA and several environmental organizations. Under this agreement, EPA is undertaking a program to determine which contaminants out of a list of 65 allegedly toxic compounds and classes of compounds are present in the effluents of 295 industries in 21 major categories, including petroleum refining. As a result of this agreement, a new task force, W-22, was formed at API. This task force was given the objectives of (1) reviewing, evaluating, and critiquing analytical methods selected by regulatory agencies for qualitative and quantitative determination of the presence or absence of trace toxic pollutants in refinery waste waters; and (2) conducting sampling and analyses for these trace toxic pollutants at selected refineries.

This task force has been extremely active since it was formed early last fall, and members and API staff have met with EPA personnel on several occasions. We have reviewed and critiqued the sampling and analytical protocol being used by EPA in its analyses of refinery and other industrial wastewaters. The task force at the present time has grave concerns about the capability of the sampling and analytical protocols to detect -- and perhaps quantify -- the presence of these toxic compounds at exceedingly low levels, and of the accuracy, repeatability and reproducibility of the methods being employed.

As Marvin Wood mentioned this morning, Kerr Laboratory personnel are presently sampling and analyzing waters from 12 refineries. These include intake waters, separator or DAF effluents, and final effluents. In addition, EPA is conducting pilot scale powdered activated carbon enhancement of activated sludge units, and granular activated carbon end-of-pipe treatment, at some of these 12 refineries. The W-22 Task Force is monitoring this effort and has also selected three of the 12 refineries for its own parallel study. Samples are being taken at the same locations and times as those taken by EPA. The samples are being analyzed for the 129 priority pollutants using analytical techniques similar to those being used by EPA contractors. In addition, more detailed and specific analyses of PNA's are being run. We feel that the results of this study will give us valuable information concerning sampling and analytical variability as regards the priority pollutants in refinery wastewaters.

Phase I of the W-20 study is presently in final review stage, and the last of the analyses for Phase II are now being carried out. As a result, no reports have been issued and many of the findings are preliminary. In addition, I should emphasize that in view of the limited number of facilities involved (two refineries and two municipalities), the study results will not necessarily be typical of either the refining industry or of all municipal treatment plants. Rather, they were carried out to build a data base where none existed.

Preliminary results from both the W-20 efforts and the W-22 refinery analyses do, however, look very encouraging. Although a few of the so-called priority pollutants were found to be present at levels greater than 10 ppb in separator or DAF effluents, even these appear to be significantly reduced in the refineries' biological treatment systems. Available results indicate that there are no significant quantities of the allegedly toxic pollutants in the final effluent samples of the refineries analyzed to date. In addition, the W-20 study revealed that there were no significant quantities of organo-halide precursors in the effluents of the two refineries sampled.

One very interesting result of both studies is that a very poor carbon material balance is obtained when comparing ppm total organic carbon (as determined by a TOC analyzer) to the sum of the ppb concentrations of identifiable, extractable organics. One would expect to find, however, high molecular weight compounds such as cell metabolites, proteins, carbohydrates, and oxygenated aromatics in biologically treated effluents and these would not be identified or measured by the analytical methods used. It is quite possible that these types of compounds account for much of the TOC in refinery effluents meeting BPCTCA and in well operated municipal treatment plants.

It would appear logical, then, that expensive, cost-ineffective technologies should not be required by regulation just because considerable TOC removals are obtained. Rather, it should first be demonstrated that the TOC removed is actually harmful to man or to the aquatic environment before removal is required.

BIOGRAPHY **Judith G. Thatcher**

Judith G. Thatcher holds a B.S. in Chemistry from Southeastern Massachusetts University. She is currently an Environmental Associate with the Environmental Affairs Department of the American Petroleum Institute. Prior to joining API in February of 1976, Ms. Thatcher worked for 10 years in the Research and Technical Department of Texaco Inc.

DISCUSSION

Ned F. Seppi - Marathon Oil Co. - I wondered if Mr. Denbo would discuss bio enhancement a little more thoroughly.

R. T. Denbo - I think the subject will be discussed thoroughly in a later formally-developed session. However, let me just mention generally what we had in mind when we set up a research project. PL 92-500 includes requirements for BAT - Best Available Technology. As time has passed, there have been a number of developments that indicate that toxics have become the important thing as far as water quality was concerned. This began to become obvious to us a couple of years back. The first question is - do we have a toxics problem in BPT treated refinery effluent? And the first step in attempting to ascertain that was the program that Judy Thatcher and Kent Drummond talked about and that was the analysis of BPT treated refinery effluents for residuals. But before the results became available we began to look for ways to get rid of compounds of concern if they are, in fact, present. We decided to look at what can be done along the line of upgrading existing bio systems. Jim Grutsch and others had done work on higher sludge ages and how effective this is in further reducing organics in treated effluent. There had been work done by many people on powdered carbon. We decided to undertake the controlled experiment that Len Crame will talk about in detail. That's what is meant by bio enhancement or enhancement of biological treatment systems.

Paul Mikolaj - Lion Oil Co. - You mentioned that you're monitoring three refineries along with the 12 that EPA is monitoring. Are EPA's results coming out the same in terms of the removal of these priority pollutants?

Judy Thatcher - We have not seen any of EPA's results to date, Paul, and we only have some limited results from our own studies right now. I was basing my discussion on what we had found in the two phases of W-20 and on our limited results to date on these three refineries. We're obtaining samples from the third refinery this week. We would hope that EPA's results come out the same.

E. A. Buckley - Lion Oil Co. - I would like to ask this question of either Mr. Beychok or Mr. Denbo. First, Mr. Beychok, I assume that you will cover the injection of caustic into sour water strippers. My question is: at the present time, do we have enough information to use caustic injection in a stripper being built now?

M. R. Beychok - A preliminary report on SRI's work covering that subject was given at the API meeting in Chicago a few weeks ago. I think that SRI did a very good job of quantifying that the optimum caustic injection point is at the top of the stripper with the feed. They also defined the amount of caustic required. That report is available to you to use now. The final report may not be issued for some months, but the preliminary report is available and provides enough information to be used now in designing for caustic injection.

William C. Galegar - R. S. Kerr Environmental Research Lab - I would like to turn around the question that was asked a little earlier this morning. If I include Mr. Beychok in the group sitting at the table, you broadly represent the group that we have turned to for handling the research programs that have been undertaken to provide answers. The question I would like to ask the group is: are the research programs related to the refining industry wastewater treatment providing adequate information? If not, how can they be improved? I am talking to your group as a whole since you represent universities, industry and consultants.

M. R. Beychok - I'll give everyone a chance to catch their breath while I try to respond to that as an individual private consultant. My opinion is somewhat as stated earlier by Bob Denbo. We've worked the problems of refinery wastewater technology quite a bit and I think we now have a good data base. My experience with some of the research programs such as the SRI work for the API and the Carnegie-Mellon work for ERDA indicates that our emphasis and attention should now be devoted to laboratory analytical procedures. We haven't defined those procedures well enough yet and there are many problems with procedures that we've always considered well-proven and adequate. We don't yet really know how to analyze for ammonia or for cyanides. At least, that's what SRI found out. Dave, do you agree with that statement?

Dave Bomberger - Yes, I think so.

F. S. Manning - The RSKERL has measured the analytical variability of 5 wastewater parameters for refinery effluents. This data can be obtained from EPA Document 600/2-76-234 (September 1976).

Arthur J. Raymond - Sun Oil Co. - In your talk you talked about your analysis of polynuclear aromatics and chlorinated hydrocarbons. You said the EPA used gc-ms, what methods are you using?

Judy Thatcher - Well, the W-20 study was started before the toxic settlement agreement and before the EPA sampling protocol came out, so we used a variety of methods. The PNA method was developed by Exxon R&E and involves solvent extraction, clean up of the sample over an alumina column, elution, separation of individual PNA's by gas chromatography, trapping of each peak, and quantitative measurement by UV spectrophotometer with results based on ^{14}C labeled internal standards. For the organo-halides, that involved purging of the volatile organo-halides and passage through a gas chromatograph. The detector was a microcoulomenter which only measures halogenated hydrocarbons. The volatile organics were purged from the sample and analyzed by gc; the non-volatiles were solvent extracted, I think mainly by carbon tetrachloride. There was some preliminary gc-ms work done on the non-volatiles. With regard to the W-22 studies, we have Radian Corp. who is running the gc-ms protocol as specified by EPA. We've made a couple of changes, one involves the final effluent samples from each one of the refineries. We'll be spiking each sample with certain of the pollutants. As far as I know EPA is not doing any spiking of the actual water samples. We will run a final effluent sample and then spike a duplicate of this, and run that and try to get some feeling for the accuracy of the method. And then in addition we're looking at polynuclear aromatics by the Exxon method which can measure, I believe, up to 18 individual PNA's. We know already from preliminary results that the gc-ms method in the protocol does not separate all the PNA's and so you end up measuring three PNA's under one peak.

SESSION III

OPEN QUESTION AND ANSWER SESSION

INDIVIDUAL PROBLEMS IN MANAGEMENT OF REFINERY WASTEWATER

Chairman

*Francis S. Manning
University of Tulsa
Tulsa, Oklahoma

Panel Members

Milton Beychok
Consulting Engineer
Irvine, California

W. Wesley Eckenfelder
Vanderbilt University
Nashville, Tennessee

Davis Ford
Engineering Science, Inc.
Austin, Texas

H.E. Knowlton
Chevron Research Company
Richmond, California

R.N. Simonsen
Standard Oil Company of Ohio
Cleveland, Ohio

*Biography on Page 52

OPEN QUESTION AND ANSWER SESSION - INDIVIDUAL PROBLEMS IN MANAGEMENT OF REFINERY WASTEWATER

Milton R. Beychok
Consulting Engineer, Irvine, California

W. Wesley Eckenfelder, Jr.
Vanderbilt University, Nashville, Tennessee

Davis L. Ford
Engineering Science Inc., Austin, Texas

H. E. Knowlton
Chevron Research Company, Richmond, California

R. N. Simonsen
Standard Oil Co. of Ohio, Cleveland, Ohio

N. Seppi - Marathon Oil Co. - I would like to ask Mr. Eckenfelder if he would discuss nitrification and go into the prevention of upsets which result in loss of nitrifying bacteria and possibly talk about methods of recovery from the loss of nitrifying bacteria.

W. W. Eckenfelder - Our experience to date has tended to indicate that dependable nitrification plus carbonaceous BOD removal can be achieved in the treatment of domestic wastewater in one stage. Highly variable success has been attained on most industrial wastewaters. Nitrification is better considered in a second stage after removal of inhibition in a first stage. The second stage could be either activated sludge or rotating biological contactor or an up-flow aerobic filter. It also appears that the use of powdered activated carbon in the activated sludge process tends to greatly enhance nitrification. The carbon tends to remove compounds and materials which would tend to be inhibitory to the nitrification process. The case to which I refer while not a petroleum-refining effluent, indicated that straight nitrification required an average sludge age of about 45 days and that with the addition of the powdered activated carbon, was reduced down to about 8 days. Again, of course, there is an economic trade off here, but apart from the economics, having a greater dependability of operation would mitigate towards powdered carbon or possibly towards a two-stage process as opposed to one.

Davis Ford - I think the question was asked regarding recovery of nitrifiers, and it is a difficult question, but I might communicate one or two things. The first step, and we've had some experience in this area, is if you have low nitrification periods which had been preceded by good nitrification, temperature may be the problem because as you know nitrification tends to drop off in winter climates. When lower temperature prevails, we try to reseed from plants which have had good nitrification. We've done this down in the South Texas area with some success. Of course we know all the other environmental factors which we can correct, namely the pH sensitivity, the sludge sensitivity, and I certainly agree with Wes on the sludge age. Take sludge age and look at some of the old graphs and we expect certain percent nitrification that just isn't there. And that's particularly true when you have a high concentration of organic nitrogen, TKN, particularly amines. I think in plants wherever applicable, control of amines could be an answer to nitrification in biological processes. And of course, the third response as far as correction goes is to get a good lawyer. We get into very strict ammonia nitrogen concentration requirements on NPDES permits. It is my opinion that many of the permits that go into effect on July 1, 1977 are going to be noncompliant in terms of ammonia. So it takes the combination of a lot of negotiation with regulatory authorities and some of the steps I outlined.

Eldon Rucker - API - There was some mention this morning about the fact that the refining industry appears to be well on its way to solving many of the problems of the priority pollutants. I wonder if any particular members of the panel, or the entire panel, might comment on whether some of these problems could be transferred into the sludge, and if this is the case, what are the accepted methods for handling sludges generated in refineries?

H. E. Knowlton - As a member of the API Solid Waste Committee, one of our concerns is the new Resource Conservation and Recovery Act which affects handling and disposal of oily sludges. Many people recognize that land farming is an excellent way of treating oily solids and biosolids. Land farming of oily solids and biosolids done properly will not put contaminants into the ground water, there is not a run off problem because you normally dike these installations so any net water is put back into the wastewater treatment system. The studies so far show that the net water from a land farming area has very low amounts of contaminants such as oil. We also believe we should recover as much oil as economically feasible so that the amount going to land farm will be relatively small.

Davis Ford - I might just make one comment with respect to sludges from refineries. Speaking now as a consulting engineer, you start off with land farming and then back off. Because of process applicability in many areas in the U.S., successful land farming can be achieved for oily and biological sludges. Now this normally forces digestion to satisfy most state regulations, then combining with biological sludges, and then to land farming. Another comment is that the key here is dewatering. I think technology has certainly progressed a long way in dewatering of oily sludges. I know that EXXON and others are having good success with belt filters, so if you can successfully dewater through belt-press, or other filters, or other comparable processes, and combine that with the digested activated sludge, land farming is the place to start. This is far better than less palatable methods such as incineration, so I think that's our starting point.

E. A. Buckley - Lion Oil Co. - On your land farming of the sludge, how do you determine how much oil you've got say in an alum sludge where you're coming off a DAF system? Of course you have floating oils which you can separate, but how about separation of the alum sludge?

H. E. Knowlton - My answer to you is that at Chevron we don't have any alum sludge. And we don't have any for a very real reason. About 3 or 4 years ago we said, let's go to the new induced air flotation process; we don't want the problem of handling-disposing of that sloppy mess. And it is a mess. So we don't have this problem and I can't give you any solutions for a non-existent problem.

N. Seppi - Marathon Oil Co. - What's a rule of thumb as far as the barrels of oil per acre that you can soil farm?

H. E. Knowlton - In a recent paper on land farming prepared by Sun Tech and given at the CREC meeting in Chicago, they were land farming 600 barrels of oil per acre per year. I think the answer is, where are you? If you're in an area where it's quite warm such as in Southern U.S.A. where on a hot day (95°F) we measured 130°F one inch down in our soil of the land farm, then you can expect the oil to biodegrade rapidly. This assumes that your land farm is set up properly. In the northern areas obviously your working time is shorter and your temperatures lower, so biodegradation potential per acre is less.

Ben B. Buchanan - Phillips Petroleum Co. - I would like to ask the panel if they could comment on the revolving disc biological process as compared to activated sludge, and if they know of differences in the types of bacteria used for both processes? Of course the slime forming bacteria and the revolving disc process I don't know how different they are from the activated sludge bacteria. Can you have nitrifyers in both systems, or are there limitations to what bacteria on revolving discs can do compared to what they do in activated sludge?

R. N. Simonsen - We have had pilot plant experience at one location having a well operated aerated lagoon system with several days aeration time. We are interested in getting nitrification and ran both activated sludge and rotating biological surface pilot units using aeration basin effluent for feed. Although we got effective nitrification with activated sludge, there were frequent upsets and recovery was very slow. The RBS unit in the same application worked quite well. We don't know what differences in bacteria type there may have been. Dave Rulison who is in the audience and did the work might comment further.

Dave Rulison - Sohio - Only that in the case of activated sludge the variability of the feed coupled with the difficulty in retaining nitrifyers in the system meant that small upsets would ruin nitrification. With the RBS unit, even significant changes in feed quality didn't make much difference.

H. E. Knowlton - One of your questions was comparison of activated sludge vs. biodiscs. To answer that, in six Chevron refineries, one is using activated sludge, two are using biodiscs and three are using ponds. The criteria used to pick a biosystem for these individual situations was which system will cost the least. I will make one comment on what we see with one of our biodisc systems that went on stream about December 1976. A month ago an operator dumped 11 tons of acid into the system. This was not discovered until morning, by which time the acid removed most of the biosolids from the eighteen 11 foot diameter by 25 foot long discs. The acid cleaned those discs of that material. The item that really made us quite happy was that at the end of two days we were back meeting our phenol spec. In other words the discs had recovered sufficiently so that we were meeting our phenol specification in the final effluent. We thought this was quite remarkable, because of the severity of the upset. We have found by other experiences that of the contaminants removed in the biodisc process that phenol removal is the last to recover.

Davis Ford - I would like to make a few comments on the RBS-activated sludge comparison. Let me use RBS (rotating biological surface) because "Bio Disc" is a trade name and I don't want to advertise. Let me say that I have personally come to full cycle about 4 or 5 years ago, inherently I was rather negative on the whole RBS concept. I think today I have a much different view about that. Chevron Research was partly responsible. Let me make a few specific comments, and I'll discuss that in more detail Wednesday morning. First of all, from an operator's point of view and from a cost point of view, RBS or bio disc has a lot of innate advantages, mainly on power-connected horsepower as compared to activated sludge. It's much simpler to operate, and I think the capital costs with BOD's below a certain level - I'm not sure what that level is - but capital costs are probably more cost-effective or cheaper than the activated sludge. I don't want to make these positive comments at the expense of activated sludge; that's been the "modus operandi" in the petroleum refining industry for a long time and it's really the basis for BPT and will probably be the basis to some extent for BAT in the remaining guidelines. I believe that as the influent BOD gets higher, let's say 750 mg/l or higher, then activated sludge might be equally or more attractive than RBS systems. Again, I don't have specific numbers for this but when you get into high BOD's you'd better check the cost-effectiveness quite carefully before making the process decision. We designed both RBS systems and activated sludge so we have no inherent process bias. But let me make a few comments on questions that I still have about RBS systems. One, I think you have to be careful when comparing the ability to withstand upsets between RBS and activated sludge because you're getting full raw waste load impact on those first discs; for example, an acid spill. Whereas in a completely-mixed activated sludge system the acid equivalent or potential bio-toxic or bio-static level per bacteria is reduced, it is less than in RBS systems. I think the jury is still out on the ability to withstand upsets, recognizing too that you have the ability to operate at very high sludge inventory on any activated sludge system, and you kind of ride the line on the RBS system. It has been proposed, primarily by the vendors, that sludge settleability in RBS systems is better than that of activated sludge. I think that would be the case, although I have yet to see it proven. So, I still have a question on the effluent TSS ability of an RBS system as compared to activated sludge. With respect to BOD less than 750 or 500 mg/l, we found that activated sludge systems take out about 1.5 to 1.6 lbs of BOD per horsepower hour. If you can use that parameter to determine the power efficiency or power utilization removing BOD, whereas RBS systems on the paper studies that we have done preliminary to the detailed design have been about 2.3, so it is more energy-effective. At low BOD concentrations you have an inherent incentive to consider RBS systems, particularly in land-limited situations. One other comment - RBS has been proposed by the organic chemicals industry and we're a bit reticent to accept that system carte blanche when you have COD problems because your contact time between the bacteria and the sludge in RBS systems is going to be less than it is, for example for extended aeration. You can solve the BOD problem but possibly not the COD because the hydraulic contact time is quite low. There is no way to accurately calculate sludge age, which you can of course in an activated sludge system. One quick comment on nitrification - I believe that the RBS system offers advantages in nitrification as compared to activated sludge, because of the ability of the latter stages in the RBS system to develop a good nitrifying bacteria. And also, it has been quite successful in adjusting the pH, raising the pH in the latter stages to the optimum level for nitrification.

Bill Ruggles - Phillips Petroleum (Bartlesville) - With the increasing emphasis on hydrocarbons in the atmosphere, I am wondering if any member of the panel has experience with possible effects on this situation that has resulted from the land farming of sludge?

H. E. Knowlton - There are no numbers available on this to our knowledge. In fact, one of the items on the API budget for next year is to measure hydrocarbon emissions from a land farming area. We expect very little as we've spread oily sludges and rototilled them in and have not been able to smell any odor in the area.

E. A. Buckley - Lion Oil Co. - One other question. What are the most feasible as well as most economic ways of reusing treated wastewater?

M. R. Beychok - There are literally hundreds of answers to that question and they are all refinery or site specific. The first answer that comes to mind is the reuse of treated wastewater as cooling tower makeup. Another answer is the reuse of treated wastewater to produce low pressure steam (rather than high pressure steam which requires relatively pure water to avoid excessive and uneconomic blowdown). The low pressure steam might be used in atomizing the oil fired in process furnaces, or as flare steam, or as stripping steam in crude unit sidecut reboilers and in other process steam uses. Using treated wastewater for low pressure steam generation may require 10-15% blowdown to avoid fouling problems in the steam generation units. If you attempt to reuse treated wastewater for high pressure steam generation, you can't afford such high blowdown rates and you will need tertiary treatment following your secondary treatment to make the water suitable for high pressure boiler feedwater. As you may know, the API CREC funded a pilot program studying the reuse of treated wastewater in cooling towers to take advantage of the evaporation in the cooling tower so as to result in a more concentrated waste in the form of the cooling tower blowdown.

E. A. Buckley - Lion Oil Co. - What parameters would you put on the TDS in evaporated cooling water blowdown?

M. R. Beychok - It depends upon the cycles of concentration at which you operate the cooling tower. It also depends upon the economics and whether you can justify a slip stream filter or a slip stream softener on the circulating cooling water. Some refineries have so-called "clean water" and "dirty water" cooling towers which adds another parameter of flexibility for reusing treated wastewaters.

H. E. Knowlton - I can give you an example of reuse recently completed which worked out a lot better than we hoped. This refinery had 800 GPM of effluent; it now reuses 400 GPM of filtered effluent 250 GPM into the cooling towers and 150 GPM into the process water fire-water system. We've been running only a month and a half or so but this has worked out very well. We see no problems so far and the effluent is reduced to 400 GPM. We do not have a lot of analyses as yet to tell us if anything is unusual, but we don't see anything. Also we're surprised, we thought that maybe the calcium might double but so far we can't see it changing much. Some things happen in a practical system that when we plan we don't anticipate. Other refiners, by the way, have used API-separator water in their process water and fire water systems for 25 years. Their water is very poor quality compared to that we are reusing which has a BOD of less than 10 PPM and an oil and grease content of less than 10 PPM.

R. N. Simonsen - We have used effluent in fire water systems, but I should relate what happened when this was tried at one refinery which has since been shut down. Effluent had been used to pressure the fire water system for several months. Then, during a plant fire fighting training exercise, attempts to extinguish a fire with a foam generator failed because the powder would not make foam. New powder from the storehouse also failed to make foam. This was how the refinery discovered it had been operating several months without fire foam protection. Neither we nor our supplier ever learned why and, of course, the refinery changed back to its former fire water supply. A number of refineries use stripped foul condensate and blowdown from oily cooling towers in desalters as another form of recycle.

M. R. Beychok - This isn't another specific example, but rather a general caution. When designing any process unit, you must be very careful about recycling. You must avoid a closed loop from which there is no way to bleed out any buildup of a recycled impurity. The same thing holds true for reuse of treated wastewater. You don't want to recycle in such a manner that you create a closed loop and build up an intolerable level of dissolved solids or other contaminants. So you want to thing in terms of cascading systems. If your treated wastewater originated from steam condensate, reuse it to generate steam which will be used in other services. Or if you reuse the water in a cooling tower, be sure not to lock yourself into a closed loop which has no way to bleed out or blowdown impurities.

Ed Sebesta - Brown & Root, Inc. - I would like to go back to the subject of biological rotating discs reactors, and mainly some comments on the maintenance - good or bad, on some of these systems that have been in operation for some time.

R. N. Simonsen - We haven't had any maintenance problems since our full-sized RBS units haven't been installed yet.

H. E. Knowlton - We have had one in operation for about 2½ years, it's a styrofoam disc unit. We've had a few things happen, like the carbon steel nuts on the ends of tie rods corroded off, and then the styrofoam discs moved out of position. One of the problems with rotating disc units is that people tend to never look at them. It sits there and runs with very little attention. Mainly one tries to control feed quality to it because what you put in determines what comes out. So the main effort is to keep a reasonable plant control on your input quality. We suggest now that every three months they go in and actually check each disc and make sure that nothing is wrong. There should also be some surveillance. The operator should walk by each of the discs once per shift to see if there is noise or anything indicating a problem. A second unit we have in operation has been operating roughly six months. We see no problems there; it is a large system of 18 shafts. There was a recent NPRA paper on rotating discs; (AM-77-27), Refinery Use of Rotating Biological Surfaces in Waste Water Treating. In this paper we gathered the available information on four existing commercial size installations that were processing refinery waste water in the U.S. in February 1977. You can ask Herb Bruch, NPRA Technical Director, for a copy. There is a fair amount of detail in it on this subject. Are there any other questions on this one?

Ed Sebesta - Brown & Root, Inc. - A follow up while you're up. When you did have that problem with the one at Salt Lake City, to redo it how did you operate while you're doing repairs, or what did you have to do to repair it?

H. E. Knowlton - They stop the rotation and bypass the water to the next shaft. Then they patched the styrofoam discs that were torn. You can by-pass these things. This system is set up with four shafts in a row and has two rows; if necessary you can by-pass a whole row, but normally it isn't necessary to do that, you can just by-pass the one involved and work on it.

L. D. Erchull - Union Oil of California - I'd like to address this question to the panel as a whole. On nitrogen removal from refinery waste water streams after they have been steam stripped, are there any installations that you know of where some proven technology has been applied where it can work year round, say in the northern climates of the country?

R. N. Simonsen - Are you talking about treating stripped foul condensate by itself? We haven't tried that, but nitrification of refinery wastewater containing stripped foul condensate can be accomplished with the RBS in northern Ohio. But temperature is very important and the colder it is the more surface is needed.

Davis Ford - I would like to add one more comment to that. I mentioned a case history where the nitrification has been consistently 85%. I might mention that the ammonia coming in about 10-15 g/liter, that's a pretty low concentration for a raw waste load going through a biological system just to put that in perspective. I'm not sure that we could get that much nitrification if we had higher concentrations coming in. Another thing that we haven't mentioned yet on the RBS activated sludge system is that you've got to remember that the heat loss in an RBS system is much, much less than in activated sludge, which is in effect a cooling tower with mechanical aerators. So, that would give us an added advantage on nitrification which is so temperature-sensitive in the northern climates, using RBS compared to activated sludge. With respect to pH, it has been indicated that about 7.5 lbs of alkalinity as calcium carbonate is destroyed per lb of nitrogen nitrified. I think perhaps we would have a little better pH control in an RBS system using the approach I discussed earlier where you add alkalinity to the latter stages that have already experienced an initial pH drop through the production of CO_2. So even though you have a pH problem in both activated sludge and RBS, you might have a little more positive control on the RBS system by controlling pH through the various stages.

W. W. Eckenfelder - I think one of the benefits of the rotating contactor for nitrification as opposed to activated sludge stems from the fact that you will generate roughly 50 lbs of bio mass per 100 lbs of BOD removed, but only about 15 lbs of bio mass per 100 lbs of nitrogen oxidized. What this means is in a completely-mixed activated sludge where both BOD and ammonia are to be oxidized the population of nitrifyers is going to be very very low; in the order of probably 1 to 4%. In a rotating contactor, admittedly in your initial stages where you are primarily rmoving carbonaceous organics you will have a very very low population of nitrifyers, but once the carbonaceous organics are essentially gone, then 40 to 50% of the bio mass will be effective nitrifying culture. This provides a cushion against both changes in concentration and also changes in operating temperature. Where nitrification is important, and this refers to my earlier comments on one stage vs multistage activated sludge, that you should consider the relative concentration of nitrifyers as opposed to the concentration of other organisms. With respect to pH, 7.15 lbs of alkalinity are required per lb of nitrogen oxidized. Normally the amount of nitrogen to be oxidized should not probably pose a major pH problem. But it could be a problem if the available alkalinity is low and your amount of nitrogen to be oxidized is high.

H. E. Knowlton - I would like to make a comment to the Union man. If we find we have an ammonia problem we go back into the process units and find the ammonia sources. Then we can strip it better; or reduce the volume of the stream before stripping it. We've done both and we end up with a significant NH_3 reduction. We also find high content NH_3 streams going into waste water treating from sources not previously recognized. We of course send them to NH_3 recovery.

M. R. Beychok - Well, Buzz beat me to it because he didn't play tennis this morning and he can get up faster than I can. But I want to second his comments. I think that very few refineries really have good nitrogen balance data across their wastewater systems. The first thing is to find out where your ammonia is coming from and find out what ammonia containing streams are bypassing your stripper. Then you should provide better ammonia stripping or reduce the volumes of those streams or both. The end-of-the-pipe treatment for nitrogen ought to be a last resort.

Davis Ford - Just this comment - I don't want to mention names, but there certainly are plants. One plant in particular that I'm thinking about was not designed for nitrification but its nitrification level has been consistently at about 85% through the whole 12 months. It is in the Southern part of the U.S. so the temperature is favorable. Right next door, however, there is a problem in nitrification. To get back to my earlier comments, there are so many variables - specific toxicity of certain organic compounds, etc. - so that it is just not that predictable. But there are case histories of good nitrification throughout the year. You're from Union, I guess. I know when you get up around the Chicago area and you have a significant drop in temperature, that tends to play havoc with nitrification systems - and I'm talking now of just around 15, 10, or 8 °C.

Bob Carloni - Lion Oil Co. - We've just recently put on a treatment plant which uses a mixed media gravity filter and we weren't getting very good solids removal until we started using a polyelectrolyte. Is that normal experience? If it is what sort of concentrations of polyelectrolytes should we be considering? We're currently using 2 ppm and we've heard that we should be down to around .5 ppm or lower.

Davis Ford - What type of system are you talking about?

Bob Carloni - This is a filter which follows a clarifier which follows an RBS system.

Davis Ford - The first comment is, yes, polyelectrolyte is being used to keep people out of jail all over the country right now. Concerning control of effluent TSS levels without filters, and I can cite you example after example, it is not free. In some cases the concentration requirements are 2, 4 and 5 mg/l and I know the polyelectrolyte salesmen are going to be happy. It is about \$1.00 - \$1.50 per lb, so if you have a high flow it's an expensive operational procedure. It's been working quite well, however, just for final clarifiers where just the poly is added to the activated sludge or RBS effluent and is mixed going to the final clarifier. With respect to post filtration, it is my opinion that you have got to have at least a poly addition capability prior to post filtration. Once you get into the operation you might want to back off, but as a capital expenditure you'd better have the ability to add a coagulant or coagulant aid to enhance filtration. By the way, the enhancement of effluent TSS quality by virtue of adding poly, which is normally 1 - 1½ ppm, but sometimes a little higher, has often been around 30% to 50% improvement in equivalent TSS.

H. E. Knowlton - Chevron has only one refinery with a filter on a final effluent. On this one final filter we do not use polyelectrolyte. As I recall we get roughly a 50% drop in BOD. We possibly could get more removal with polyelectrolyte but we don't use it because we have no need. We see these results of the filter--approximately 50% oil reduction, and 30% BOD reduction. We run this filter on a time cycle only because we find that the ΔP control system was not practical.

R. J. Churchill - Tretolite - We're one of the polymer companies that are getting rich according to Davis. Polymers are useful but only as a tool. They are not a panacea.

We've been called into places where people have bulking type problems and ask us to add a polymer to solve that. You're treating a symptom you're not solving a problem. We have had success in the application of filters by going into the clarifier, that is adding to the mixed liquor on the way to the second clarifier, which does two things. One, it knocks down the TSS leaving the clarifier going to the filter; second, almost uniformly or almost characteristically we have seen it knocks down the variability so that you don't slug the filter with a high TSS concentration episodically. That does two things and it reduces the total solids load put onto the filter which should extend your run life. It should also then give you better net TSS out of the filters since you're starting with a lower TSS in. It also may turn out to be more economical to go to a split addition rather than trying to do it all in one step. I think the key to the polymer is simply to use it as a tool that is to take out the fluctuations and the total amount of TSS leaving the clarifier going to the filter. To answer the point about one-half a part or 2 parts or 10 ppm, we've treated systems with less than a part very low concentrations at the secondary clarifier. We've also treated refinery systems as high as ten parts at the secondary clarifier. I think that relates back to some of the points that Buzz was mentioning. You can have bulking or nonsettling type sludges that's not a problem to be solved by a polymer. You can oil carry over into your biological system and into the clarifier which affects settleability. Again, that's not a polymer problem. It's a process problem or a waste management problem. I think it's hard to draw any hard fast rules but excluding my bias I do think it's a tool, but it's a tool that only can be used wisely.

Rich Sheridan - Brown and Caldwell - I think it was Mr. Ford that mentioned the appropriateness of the bio discs in situations where nitrification would be required in cold climates and therefore the bio discs have the advantage of less heat loss. I would like for someone to comment on the requirement to nitrify in cold climates, as to its appropriateness, cost effectiveness, these types of things.

W. W. Eckenfelder - I think it's obvious to all that in most cases involving cold climates, as far as water quality goes, nitrification is neither justified nor is it required. My own opinion is that these cases should consider a two tiered permit in order to avoid a large economic penalty for nitrification in cold weather conditions. As far as water quality goes, the fact that the process of nitrification radically slows down in the treatment process, it equally slows down in the receiving water.

Eldon Rucker - API - In view of the existing widespread use of lagoon systems in the refining industry, would the members of the panel comment on the efficiency of these systems compared with some of the RBS and activated sludge which have been previously discussed?

M. R. Beychok - It depends upon what sort of lagoon system you're talking about. I will be very specific and talk about surface-aerated systems using mechanical aeration as against those that depend simply upon photosynthesis. I'm talking about lagoons with 3-4 days retention, 12-15 feet deep, and using up to 50 hp per million gallons of retention for mixing and aeration. About 4-5 years ago, an AIChE committee surveyed existing aerated lagoons in the refining, petrochemical and the pulp and paper industries. I don't know if Wes Eckenfelder remembers it or not, but one of his colleagues reviewed our final conclusions from that AIChE survey and disagreed with us. In any event, the data showed that 85-90% BOD removal could be achieved in those lagoons, within the parameters mentioned: 12-15 feet depth, 3-4 days retention and up to 50 hp per million gallons of retention. That contrasts with about 90-95% BOD removal for activated sludge systems. I'm not sure what the average percent BOD removal in an RBS system is, but I would imagine it is somewhere between the aerated lagoon and the activated sludge systems.

W. W. Eckenfelder - I think one thing is pertinent and that is where you have an aerated lagoon system, or a waste stabilization pond, you are going to be much more subject to temperature effects during the colder weather than you would be from either an RBS or activated sludge process. The variability month by month would generally be higher from an aerated lagoon than it would be from those processes that tend to minimize heat loss during the colder climates. I would agree from all of the data that I have seen that a properly designed and operated aerated lagoon process should be capable of doing about the same thing as the other processes relative to BOD removal. One of the obvious problems with an aerated lagoon is the effluent suspended solids.

M. R. Beychok - To further qualify my earlier answer regarding 85-90% BOD removal in aerated lagoons, we adjusted for the variability of temperature by using a power law function. We converted all of the data to a base temperature of 77 °F. We also recommended that aerated lagoons be designed for the coldest temperature in order to achieve the required BOD removal during the winter. Then one could take advantage of the oversized system capabilities during the summer months to schedule maintenance and turnarounds.

John C. Doolittle - Shell Oil Co. - Relative to the aerated lagoons, what effect would an occasional oil film on the lagoon surface have upon BOD removal?

M. R. Beychok - I suspect it would depend upon whether you have 15 hp or 50 hp per million gallons of retention. The key thing in my opinion is mixing and not aeration. A high degree of mixing will offset any effect that an oil film might have on oxygen absorption. 50 hp per million gallons of retention will more than provide the oxygen required.

H. E. Knowlton - Eckenfelder said that the lagoon system is very dependent on temperature. And in certain areas of the country the lagoon system wouldn't be effective. This also has been our experience. In the southern part of the U.S. or Hawaii we find that the lagoon system is excellent even though we have some TSS problems. In fact in one refinery we exceed comfortably "77" permit conditions with a lagoon system. I would like to mention that in the first refinery in the U.S.A. to use biodiscs, we did have a lagoon system. The only reason we put in biodiscs was that in the winter time when the effluent water was 33 °F, we couldn't get enough BOD reduction. We put in the biodiscs and even though the water into the biodisc is at 50 °F, it drops only about 1 °F at an ambient temperature of 20 °F. In our second installation during the severe cold weather of last year, we saw only a 6 to 8° drop across the bio disc system with ambient temperatures of 0 °F which is a pretty minimal drop. We did not suffer at all from the severe cold weather. This is one of the pluses we see for bio discs.

Davis Ford - I have one other comment on the aerated lagoon waste stabilization pond. I'm not really sure that your question is on waste stabilization ponds or aerated lagoons, but let me add a postscript to the aerated lagoon discussion. I really agree, and sometimes it's difficult to convince regulatory authorities, that the aerated lagoon system is a BPT system in many cases, and I really believe that. Of course, this depends on your raw waste load and how far under the guideline number you are on RWL. The TSS comes back to haunt us. It's going to be interesting to see how the TSS numbers come out in the remanded BAT guidelines for the petroleum refining industry in September or October, because that's really the key to how applicable these systems are going to be. In many cases an aerated lagoon or waste stabilization pond concept can produce, from refinery wastewater, a much lower COD than can an activated sludge system. So there are inherent advantages. We just have the problem of algae proliferation and biological TSS to contend with, and in effect the remanded guidelines and the implementation thereof will dictate just how applicable these systems are. In addition of course we have some pH problems with waste stabilization ponds; 6 to 9 being the normal pH on those permits; and as we undergo photosynthesis using CO_2 the pH goes over 9. We have been successful, and others have too in some cases, in having a time stipulated on the permit as to when the pH is to be taken, namely, early in the morning to exclude that CO_2 utilization by algae.

E. G. Kominek - Environtech Corp. - It is apparent that there is a lot of interest on the part of this group in discussing nitrification, and it has been my experience recently that in many areas that denitrification is becoming more and more of a problem. Is this something, in the opinion of the panel, that the refineries have to be thinking about at this time?

Davis Ford - I don't think so unless your effluent discharges into a drinking water source so that you'll have to comply with the Safe Drinking Water Act which has, I believe, a 10 mg/l as N maximum. If you discharge into a body of water that is used for drinking water it could be a problem. None of the permits we're involved with have nitrates on it and I don't anticipate any. So given that drinking water exclusion I don't think you'll have any problem there.

R. N. Simonsen - One other comment on aerated lagoons. I believe the results of a recent API survey on cyanides in refinery effluents shows that the lowest concentrations are from refineries with aerated lagoons or long residence time oxidation ponds. This parameter is one of the 129 toxics and could become a serious problem for refineries discharging to low flow streams.

F. J. Kuserk - Texaco - We have an activated sludge system that does a very good job with most parameters, except we do have one problem with it. It seems to increase the one pollutant, hexavalent chrome. I was wondering if one of the panelists could tell us what's happening here? We're coming out of our API separator at hexavalent chrome levels of less than 20 parts per billion, we go through our waste water treatment plant and we're coming out in the range of 60 to 80 parts per billion.

M. R. Beychok - I don't have an answer to that. In fact, it amazes me because I recall that the API-EPA 1972 raw waste characterization surveys actually showed a decrease in total chromium and heavy metals across activated sludge units. Are you in effect saying that some total chromium is being created?

F. J. Kuserk - No we're not creating total chrome we're just going from the trivalent state to the hexavalent state.

Robert Carloni - Lion Oil Co. - Are any of the panel members familiar with any installations using ozone to improve the treatability of refinery waste waters?

R. N. Simonsen - I don't know of any in the U.S., but when Cities Service operated their Trafalgar refinery in Ontario, ozone was one of a great number of treatment steps used. I don't believe ozone is being used there now.

Ralph Churchill - Tretolite - Could I get some discussion from the panel relative to the chrome problem and the alternatives to meeting chrome guidelines, namely chrome removal from cooling tower systems, or closer control of chrome in cooling towers, or non-chromate inhibitor programs?

H. E. Knowlton - Ralph, I can tell you what our status is. We do not see any problems with hexavalent or total chrome contaminant levels in our effluents. The hexavalent chrome is reduced and total chrome removed by our waste water treating system operation. So we don't really see the need at this point of changing corrosion inhibitor or installing chrome removal systems. Especially if we can reduce our final effluent to a trickle, in the future, which we feel is desirable to get out of the clutches of EPA.

R. N. Simonsen - We have a refinery and a chemical plant side by side at one location. Both have similar water supplies and cooling towers and both used chromate inhibitors. Chromium is reduced and seems to drop out to some extent in the refinery system and is really not a problem. Chrome has been a problem at the chemical plant and it has been necessary to switch to non-chromate treatment.

M. R. Beychok - I would like to respond for those cases where you do have a problem. For example, industrial plants in California are faced with a coastal water discharge regulation limiting total chromium to 0.01 ppm (10% of time) and 0.005 ppm (50% of time). The treatment alternatives to consider include chemical reduction and precipitation which creates a gelatinous sludge which is as difficult a problem as the original chromium problem. The other alternative is ion exchange, of which there are two types which might be used. One ion exchange process is the fixed-bed type which recovers the chromium for reuse in the cooling water. Cities Service has such units in a petrochemical plant in Louisiana and I assume that they are working well. The other ion exchange process is a fluidized bed system with the ion exchange resins regenerated in a U-bend type system. As for using non-chromate corrosion inhibitors, it has been my experience that the petroleum industry doesn't think that the phosphate or zinc inhibitors work as well as chromate.

Arthur J. Raymond - Sun Oil Co. - Is there any data available on the correlation of BOD vs. TOC analysis?

Davis Ford - To answer that, yes, a lot of it but it's very site specific and many things influence that correlation. First, just the severity of the process will have one impact on the ratio and then the degree of treatment through a biological system will have another impact. So I would say in order to be substituting TOC in terms of BOD you will have to develop that correlation for your own site. You get into a lot of trouble by extrapolating that correlation to your own site and accepting a permit on that basis.

J. Dewell - Phillips Petroleum Co. - Does anybody have an experience with a new vendor process called dispersed air flotation as compared to what's called induced air flotation, and do the same chemical additives work?

H. E. Knowlton - We have a couple of these in operation. For four years we've been using induced air flotation in various refineries right after the API separator. I think the dispersed air flotation uses less horsepower. You might get slightly less removal too, but you still use the chemicals. We see it as simpler to operate and maintain than induced air flotation.

J. Dewell - What size of air bubbles do you get with the induced air flotation?

H. E. Knowlton - I haven't worried too much about that detail since the system works so well in practice.

John Byeseda - Tulsa University - I am working on induced air flotation now and in general the bubble size depends on the surface tension between the liquid and the vapor. If you've got anywhere from about ½% of salt the bubble size will be in the range of 1 mm. For dissolved air flotation you'll get somewhere around 100 microns practically independent of the interfacial tensions. And for dispersed air it's about the same size as induced air - it will be in the range of 1 mm, if there's very little salt in the water the bubble size will go up to about 2 or 3 or 4 millimeters. There is approximately an order of magnitude difference, about 100 microns.

N. F. Seppi - Marathon Oil - I had another question about soil farming. I was wondering how important is fertilization to the rate of degradation, and what effect do metals have on the bacteria degradation of oily sludges?

H. E. Knowlton - There are some Shell reports out on this, on both topics. To fix the application rate you'd have to check the soil and see how much you need. In fact in one of our refineries we did not add any nitrogen and still got sufficient activity. So, it's a matter of finding out how much is there and calculate how much you need to add if any to achieve a desired result.

John R. Kampfhenkel - Sun Oil Co. - I have a question for Mr. Kuserk of Texaco. Are your samples on the chrome taken or analyzed on a composite sample?

F. J. Kuserk - The last samples we had were done by an outside analyst.

John R. Kampfhenkel - And you got the same increase in your hex chrome? We've found down in Corpus that we were getting the same problem but we were getting it on a composite sample. It seems that we were getting a reduction of our hex Cr chrome in our sample bottles. Our influent water had a larger amount of oil in it naturally than our effluent did and we were getting reduction because of the oil in our sample containers. On a grab sample we didn't find that to be true, we found that the hex in and out was the same. I don't know whether it was just typical of our particular facility or not but we did find that to be the case in the sample container because we went back and spiked some of our samples and found that was what was happening.

Robert Carloni - Lion Oil Co. - My question has two parts. First, what is the state-of-the-art now in automatic pH control systems? And, second, would a system which consisted of one well-mix basin with feed-back control be satisfactory? In this particular situation we could tolerate a certain amount of swing in the pH of the effluent from the control system.

Davis Ford - I can't really answer that question specifically, but yes, the state-of-the-art is feed forward, feed back in pH control systems, but I have yet to see one work very well. Every time you go to the plant, the first thing the operator cusses is the pH control system, so I guess that is the state-of-the-art. A two-stage control system is good when your titration curve indicates you can fine-tune on the second stage and satisfy most of the neutralization requirements in the first stage. That probably helps. With respect to swings in the PH of biological systems, of course you're going to have a normal swing there. As for the petroleum refining industry, I believe pH compliance has not been a major problem except for the algae effects, at least in the plants I've been involved with. We have pH swings - you know what you normally have in wastewaters, unless you have an acid dump or acid spill - and you try to control it in an off-spec basin or you try to control it at the source. I just haven't much experience with pH excursions from the 6 to 9 permit limits.

BIOGRAPHY H.E. Knowlton

H.E. (Buzz) Knowlton is a Senior Staff Engineer of Manufacturing Process Engineering, Chevron Research Company, Richmond, California. He served in process design, process development, technical service and process planning at Chevron. Previous experience includes Chief Process Engineer at Chevron East Refinery, Perth Amboy, New Jersey from 1967-1972 when he assumed his present position assisting corporate refineries on environmental problems. He holds a P a Ph.D. degree in Chemical Engineering from Ohio State University. Mr. Knowlton is also a member of the API committee on Refinery Control and Chairman of the API Solid Waste Management Committee.

BIOGRAPHY Robert N. Simonsen

Robert N. Simonsen is Senior Environmental Consultant with The Standard Oil Co. (Ohio) where he has been involved in environmental affairs since 1950. He is a past chairman of API's Committee on Refinery Environmental Control, and is a member of API's Environmental Affairs Water Quality Committee. He received his B.S. in Chemical Engineering from Lehigh University.

Milton Beychok Biography on Page 300
W. Wesley Eckenfelder Biography on Page 476
Davis Ford Biography on Page 206

BANQUET

Master of Ceremony -- Dr. Allen R. Soltow
Dean of the Graduate School and Director of Research
The University of Tulsa, Tulsa, Oklahoma

Allen Soltow: "Contrary to your program, my name is Allen Soltow. I am pinch-hitting for Dr. John Dowgray, who had to attend a funeral in Kansas City. First, as representative of the University of Tulsa, it is my privilege and pleasure to welcome you to this obviously successful Open Forum and to this banquet. Before I introduce the head table, may I tell you how much the University of Tulsa values its good relations with the petroleum industry. We have taken two recent steps to expand and enhance these relationships. First, we have created a National Capital in Energy-Law and Policy Institute (NELPI). We are one of the few university institutes addressing the new and very complex field of energy litigation. Dr. Kent Frizzell, former Secretary of the Interior in the Nixon and Ford administrations, is the director of NELPI. Second, we have formed a Petroleum and Energy Research Institute (PERI) which serves as an umbrella organization for extensive research activities in petroleum production and refining. Frank Manning is our PERI director.

As your M.C. for this banquet it is my pleasure to introduce the head table. Starting at my extreme right, that is your left: -

Milton Beychok,	Consulting Engineer, Irvine, California
Judy Thatcher,	Representing the API, one of the sponsors of this symposium
Bill Galegar,	Director, R. S. Kerr Environmental Research Laboratory, Ada, Oklahoma. Bill, as you remember welcomed us this morning. Bill is also representing the EPA
Dale Kingsley,	Our banquet speaker
Herb Bruck,	Technical Director, N.P.R.A. Herb is representing the NPRA, who is, of course, one of the sponsors of this symposium
Frank Manning,	Professor of Chemical Engineering at Tulsa University. Frank is Project Director of the EPA Grant financing this Open Forum.

May I also acknowledge two other people not at the head table. Ridgway Hall, Associate General Counsel for Water, EPA, and Fred Pfeffer, of the R. S. Kerr Environmental Research Laboratory, Ada, Oklahoma. Fred is the Project Officer for the EPA Grant sponsoring this Open Forum. Fred deserves the credit for engaging the speakers at this Open Forum."

BIOGRAPHY **Allen R. Soltow**

Dr. Soltow holds a B.A. in Mathematics and Business Administration from Luther College, and M.S. and Ph.D. degrees in Economics from Iowa State University. Dr. Soltow is currently Dean of the Graduate School and Director of Research. Prior to this, Dr. Soltow has been Chairman of the Division of Economics, Acting Dean and Acting Associate Dean of the College of Business Administration at the University of Tulsa. Dr. Soltow has been most involved in both national and local community activities and also participates frequently in both local and national economic conferences.

SPEECH PRESENTED AT THE WASTE WATER SYMPOSIUM

Dale L. Kingsley
Vice President of Refining, CRA, Inc.

Thank you, Mr. Chairman, and I appreciate the honor to visit with this group tonight. It is gratifying to see this large attendance, and it strengthens my belief that we in business need to meet and exchange ideas, and to determine the best way to effectively plan and act to improve the quality of our environment.

We at CRA, and I believe the other refiners that are represented here tonight, build plants to supply energy at a competitive cost, but at the same time we realize that these facilities must operate in a manner that will not degrade the quality of air and water in our neighborhoods. Industry must be a good environmental neighbor because it is not only good business, but it is also our public responsibility. We continually meet and talk about the environment as if it were a new world, but actually the earth has been in a changing climate since its formation. It is only in the last two decades that it has become obvious that man must correct his wasteful ways if we are to have a good lifestyle in the future. Since man responds slowly to change, laws have been passed that will affect our destiny. One early law -- The River and Harbor Act of 1886 -- gently started us on the road to improved environment. The Federal Water Pollution Control Act of 1948 was another milestone along this road, and the 1972 Amendment to the Act of 1948 was the atomic blast that really got our attention. We now respond to EPA, and Public Law 92-500, and others that provide guidelines and goals that we strive to meet. The requirements on waste water quality were established to help, aid and protect you and me. But, is it really working out this way? And, can we afford this protection? I am speaking of "we" as industry, as a country, and as individuals. I suggest we immediately take a serious look at the pot at the end of the rainbow as related to the 1985 water quality regulations. I am wondering when we get there if there will really be a pot of gold at the end of the rainbow, or will it be a pot of I. O. U.s? The cost of zero pollutant discharge will not be cheap. Since this is going to be a monumental cost, who is paying the bill? I have looked for the blank check to handle our cost, and have tried to analyze who is going to honor it. I conclude it makes no difference if it is paid for by industry or by government -- in the end, I am paying for it, and I am starting to wonder how much non-pollution I can afford. Have you looked at it under this light?

Our industry sponsors a national organization known as the American Petroleum Institute. Through this membership, data are collected recapping the industry's efforts, costs, and benefits received, relative to waste water management. The API summary for 1975 indicates the U. S. petroleum industry spent 629 million dollars for waste water treatment plants, and 356 million dollars for operating costs on these plants. This is about 1 million dollars a day for operating a system that does not bring revenue to the industry. I don't know where this operating money comes from, but I feel if the industry is to survive, this fund will come from products sold. Currently the industry refines about 16 million barrels per day of crude oil. On this basis, each barrel of petroleum products sold is increased in value by 6¢ just to cover the water treatment cost, and this is only a starter. CRA has spent several million dollars in the last two years to construct waste water treatment facilities, and I am sure all of you have had comparable expenditures. Many of these facilities will meet and slightly exceed the 1977 standards, but they do not, and let me stress, do not meet the 1985 standards. It is risky to predict what construction and operating costs will be by 1985, and the degree and amount of equipment that must be purchased if the industry meets the pollutant-free effluent standards. Information developed by Batelle in Columbus, Ohio predicts the U. S. petroleum industry will be spending at least 10 billion dollars a year -- possibly as much as 17 billion dollars annually by 1985 to meet environmental regulations, and these are 1975 dollars. If the industry is processing 20,000 barrels per day of crude in 1985, the consumer cost for environmental improvement can be as much as 5½¢ per gallon on today's energy requirements, and again, this is on today's dollar. This could be inflated to 10 to 12¢ per gallon or more by 1985. The cost exposure of municipal water treating systems and other heavy industries can be equally as great, especially to the user-consumer. The Brookings Institution estimates that compliance with proposed amendments to the Clean Air and Clean Water Acts by 1985 could cost this nation at least 500 billion dollars. This number is so astronomical it is hard to comprehend, but it works out on the average to nearly $2,500 per man, woman and child in this country.

I am not proposing that we cancel our efforts to improve the environment, but let's look at it with common sense. We should continue to improve our water quality -- that is a must! but do it in such a manner that we reserve capital funds for productive industrial growth, maintaining adequate employment opportunities, and preserving our quality of lifestyles, and still have an acceptable, healthful atmosphere in which to live. This is possible if Congress and others who are directing our National commitments redirect their efforts to programs that are not wasteful, but are directionally correct, and lead us to where we really want to go. We in industry are morally responsible to provide this guidance and leadership. We need to talk to our employees -- no, not the ones in the plants, but the ones in Washington that we are supporting -- the ones whom we have elected and the ones who are working for us. I encourage you to redouble your efforts along these lines. Our responsibilities are great and it will take lots of hard work on our pant to correct the situation at hand.

You have a busy week scheduled. I wish you success in your meetings. I hope you will continue to think and direct your efforts toward the amount of pollution abatement that we can afford and really need.

BIOGRAPHY **Dale L. Kingsley**

Dale L. Kingsley, Vice President of Refining, CRA, Inc., holds a B.S. in Chemical Engineering from the University of Missouri at Rolla. He started working at CRA, Inc., a subsidiary of Farmland Industries, in 1952. He currently is responsible for the operation of CRA refineries located in Coffeyville and Phillipsburg, Kansas, and Scottsbluff, Nebraska as well as five gas processing plants.

SESSION IV

ORIGIN AND INTERPRETATION

Chairman

Marion Buercklin
Sun Oil Company, Inc.
Tulsa, Oklahoma

Speakers

Ridgway M. Hall, Jr.
"Regulation of Problem Pollutants Under the Federal Water Pollution Control Decree"

W.M. Shackelford
"Evolution of the Priority Pollutant List from the Consent Decree"

R.W. Dellinger
"Incorporation of the Priority Pollutants into Petroleum Refining"

Leon Myers
"Generating Problem Pollutants Data for the EGD Document: Refining"

A. Karim Ahmed
"Considerations for Defining Substances Hazardous to the Environment"

BIOGRAPHY Marion A. Buercklin

Marion A. Buercklin is Southwest Region Coordinator of Environmental Affairs for Sun Company, Inc. He has a B.S. degree in Chemistry from the University of Arkansas. He is currently chairman of the Oklahoma Refinery Waste Control Council and is active on several API task forces.

"REGULATION OF PROBLEM POLLUTANTS UNDER THE FEDERAL WATER POLLUTION CONTROL ACT: THE 1976 CONSENT DECREE"

Ridgway M. Hall, Jr.
Associate General Counsel for Water
U.S. Environmental Protection Agency
Washington, D.C.

I. INTRODUCTION

The U.S. Environmental Protection Agency is presently engaged in a major regulatory program under the Federal Water Pollution Control Act to limit the discharges of harmful or toxic pollutants to the Nation's waters. The strategy which the Agency devised to implement this program is reflected in a consent decree entered on June 9, 1976, by the United States District Court for the District of Columbia, NRDC v. Train, 8 E.R.C. 2120 (D.D.C. 1976), which settled four lawsuits against the Agency relating to the regulation of harmful pollutants. By the terms of this decree, EPA has promulgated toxic pollutant effluent standards for six highly toxic pollutants, and is developing effluent limitation guidelines, pretreatment standards, and new source performance standards for 21 major industries, covering 65 harmful pollutants.

The 65 pollutants were selected by an EPA task force,* assisted by outside consultants. The selection criteria emphasized primarily the carcinogenic, teratogenic, mutagenic, or other toxic properties of the compounds to humans or important aquatic organisms, as well as their presence in industrial discharges. The 21 industries were selected based upon data gathered through the National Pollutant Discharge Elimination System (NPDES) permit program, contractor reports, and other surveys indicating that each of these industries discharges substantial amounts of at least some of the pollutants on this list.

By gathering data and developing the regulations on an industry-by-industry basis, EPA expects to provide each industry with a complete package of regulations covering both existing plants and new sources, with discharges either directly to the Nation's waters or to publicly-owned treatment systems. While most of the regulations will be primarily technology based, consideration will also be given to toxicity data and potential human health effects. Where the technology-based regulations are inadequate to protect against adverse effects to human health, drinking water supplies, or the ecosystem, more stringent limitations will be set. Finally, in this connection the regulatory scheme, like the statute itself, provides for consideration of State water quality standards.

It will be the function of this presentation to describe the process by which the Agency selected the 65 problem pollutants for which it is commencing the regulatory process under the Act, as well as the 21 major industries for which these regulations are being developed.

2. STATUTORY FRAMEWORK

The starting point for any discussion of EPA's regulatory programs is the statutory framework. EPA is required under the Federal Water Pollution Control Act to regulate the discharge of pollutants into the Nation's waters. The goals of this Act include the elimination of the "discharge of toxic pollutants in toxic amounts", and, by 1985, the elimination of all discharge of pollutants into the navigable waters.

There are numerous sections of this complex 89 page statute which are designed in various ways to achieve these goals. Two of the most important sections are 301 and 304, under which the Agency is directed to develop technology-based effluent limitations guidelines by which all industrial point source dischargers are to achieve limitations by July 1, 1977, which reflect the best practicable control technology currently available or "BPT". Similar regulations must require achievement by July 1, 1983, of effluent limitations based upon best available technology economically achievable, or "BAT". For new sources, the Agency is required under Section 306 to develop standards of performance based upon best available demonstrated control technology.

These regulations are in turn applied to specific plants through permits issued under the NPDES permit program established under Section 402 of the Act. The permits are issued by the EPA Regional Administrator, or the State Director of an approved State program, of which there are at this time 27.

For "indirect dischargers", who discharge to publicly owned treatment works, the Agency is to develop pretreatment standards under Sections 307(b) and (c) for existing and new sources, respectively.

Finally, for a limited number of highly toxic and persistent compounds, the Agency may set stringent toxic pollutant effluent standards under Section 307(a) with no express requirement that technology or costs be considered. These must be met by the affected industry within one year of promulgation.

Under these sections the Agency has established effluent limitations guidelines and new source performance standards for 43 major industries, covering some 418 industrial subcategories. For many of these industries we have also issued pretreatment standards for indirect dischargers.

During the first few years of our implementation of the Act, the Agency concentrated primarily on regulating the traditional sanitary parameters: biochemical oxygen demand, suspended solids, and pH. Although certain pollutants of demonstrated toxicity, including certain organic compounds and heavy metals, were also limited, these received secondary emphasis. More recently, however, we have all become increasingly aware of the need to shift our primary emphasis to the regulation of specific toxic pollutants. This concern has been sparked not only by widespread reports of environmental damage from toxic pollutants, but also by their presence in drinking water and fish, often at disturbingly high levels, traceable in many cases to specific industrial discharges.

The Agency has also made use, albeit limited, of Section 307(a). Because that section embodies a pollutant-by-pollutant approach rather than an industry-by-industry approach, widespread use of this section would confront corporate decision-makers with a moving target. It can be disruptive and costly to industry to invest substantial sums in treatment technology for one toxic pollutant, only to be told a few months later that another toxic pollutant is to be regulated, forcing the installation of other technology which might or might not be consistent with what was installed for the first pollutant. The short one-year compliance time also imposes limitations on the use of Section 307(a), given the length of time which it takes to install sophisticated control technology.

Not surprisingly therefore, the Agency has promulgated toxic pollutant effluent standards under Section 307(a) for only six pollutants: Aldrin/Dieldrin, DDT, Endrin, Toxaphene, Benzidine, and Polychlorinated Biphenyls (PCB's). At the present time, it is expected that 307(a) will be held in reserve for those situations where the toxicity or public health threat is such that prompt and stringent control is required regardless of the availability of control technology.

In light of this experience, the Agency concluded in October, 1975, that if broad and effective regulation of problem pollutants is to be achieved, it must be accomplished on an industry-by-industry basis. This meant that the Agency would expand its use of Sections 301, 304, and 306, as well as the pretreatment authorities in Section 307(b) and (c), in controlling these pollutants.

Incidentally, this approach of using technology-based regulations to control the discharge of toxic pollutants by 1983 recently received strong support from President Carter. In his environmental message to Congress on May 23, he said:

> I have instructed the Environmental Protection Agency to give its highest priority to developing 1983-best-available-technology industrial effluent standards which will control toxic pollutants under the Federal Water Pollution Control Act, and to incorporate these standards into discharge permits.

3. DEVELOPMENT OF PRIORITIZED LIST OF POLLUTANTS

As the first step in developing a strategy for regulating these "toxic" or "problem" pollutants, the Agency decided in the Fall of 1975, to assemble a work group to develop a prioritized list of toxic pollutants which should receive primary regulatory attention under the Water Act. The members of the group included staff scientists from virtually all of the Agency's offices and divisions having responsibilities or interests in this area, with the Office of Water Planning and Standards taking the lead. Among the members were public health specialists with expertise in areas of toxicology including carcinogenicity, chemists, biochemists, biologists, engineers, and a statistician. Two outside scientific consultants were engaged to assist in the project, and additional review and consultation was provided from such sources as the National Cancer Institute and the Oak Ridge National Laboratory.

The objectives of the group were, first, to develop criteria for the selection and prioritization of toxic pollutants, and second, to relate those to the discharges of major industrial sources, and thereby derive a list of pollutants appropriate for regulation under the Act.

The group began by an exhaustive literature search, including lists of pollutants prepared by other organizations with expertise in this area. We focused our attention on both the hazard of the pollutant and the degree of actual or likely exposure to humans or wildlife as a result of industrial discharges.

The basic criteria which this task force used to evaluate the potential hazard of a toxic pollutant were: (1) evidence that the compound, or its degradation products and metabolites, pose an actual or potential health hazard, based on laboratory or human evidence that the substance produces carcinogenic, mutagenic, or teratogenic effects, adverse effects on reproduction or behavior, or adverse effects on any organ system, (2) persistence, (3) ability to bioaccumulate in organisms, and (4) evidence of synergistic propensities for these toxic effects. In addition, the task force took into consideration all available evidence that the toxic pollutants might cause lethal or sublethal effects on wildlife, particularly aquatic organisms and those species dependant upon aquatic organisms for their food supply.

With respect to exposure, we considered the following factors, wherever such information was available: (1) total production of the substance, (2) use patterns, (3) estimated extent, both qualitative and quantitive, of actual or likely point source water discharges, (4) the consequent exposure of man and wildlife to the substance or its breakdown products and metabolites, and (5) analytical methodology capabilities.

Among the more significant reports which we reviewed were the following:

> "Water Quality Criteria, A Report of the National Technical Advisory Committee to the Secretary of the Interior", U.S. Government Printing Office, Washington, D. C. (1968). ("Green Book")
>
> "Water Quality Criteria, 1972". National Academy of Sciences, and National Academy of Engineering, U.S. Government Printing Office, Washington, D.C. (1974). ("Blue Book")
>
> FWPCA Section 311 Supplement to Development Document on Hazardous Substances (EPA November 1975). EPA 440/9-75-009.

"A Report Assessment of Health Risk From Organics in Drinking Water by an Ad Hoc Study Group to the Hazardous Materials Advisory Committee," Science Advisory Board, EPA, April 30, 1975. ("Drinking Water Report")

"Identification of Organic Compounds in Effluents From Industrial Sources" Versar, Inc., EPA-560/3-75-002, April 1975.

"Final Report of National Science Foundation Workshop Panel to Select Organic Compounds Hazardous to the Environment." (Developed in conjunction with Stanford Research Institute) Dr. Norton Nelson et al., NSF, October 1975.

"Preliminary Assessment of Suspected Carcinogens in Drinking Water", EPA Office of Toxic Substances, June 1975.

"Organics in Drinking Water: Listing of Identified Chemicals Part I". Junk, et al., Ames Lab, ERDA, Iowa State University, July 1975. ("Iowa Report")

"Registry of Toxic Effects of Chemical Substances" National Institute for Occupational Safety and Health (NIOSH) (1975 ed.) and "Suspected Carcinogens" A Subfile of the NIOSH Toxic Substance List" (NIOSH, 1975 Ed.).

Oak Ridge National Laboratory Environmental Mutagen Information Center Study dated Nov. 7, 1975.

"International Agency for Research on Cancer Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man", World Health Organization (1972-1973).

"Survey of Compounds Which Have Been Tested for Carcinogenic Activity", P.H.S. Publication No. 149, USHEW.

After reviewing the work of others in this area, several things became apparent. First, while these studies provided much helpful information, none provided a direct answer to the difficult question of how to select and prioritize toxic pollutants solely from an industrial point source effluent discharge perspective. Second, our initial selection criteria mentioned above, would almost certainly undergo an evolution, or refinement, as we began to apply them to raw data and evaluate the results.

The work group began its selection process by examining as large a number of compounds with potentially hazardous effects in water as would be practical and feasible. The National Science Foundation, for example, initially looked at 337 organic compounds, later narrowing this list to 80 deemed to have the highest interest for further research. This was somewhat more helpful than the NIOSH toxic substance list, which indicates that the number of unique substances for which toxic effects information may be available is approximately 100,000.

As a starting point the work group assembled a list of some 232 compounds believed to be actually or potentially hazardous, and present in water.

After having gathered as much information as possible with respect to the initial working list of compounds, the work group determined that an initial screening procedure was necessary in order to reduce the list to those compounds requiring highest priority for in-depth review. The initial screening process employed the following selection criteria:

(1) Evidence of actual presence in effluent;

(2) Evidence of carcinogenic, mutagenic, or teratogenic effects in laboratory test systems, or human epidemiological studies; or evidence of a high degree of toxicity to aquatic organisms or systems.

Application of these criteria reduced the initial list of 232 to approximately 75. This screening procedure produced a workable group of compounds for which there was both some evidence of point source discharge and for which there was evidence of serious potential hazard to man or the environment.

This screened list of compounds and underlying data, as well as the criteria, were then subjected to further analysis and quality control evaluation. This led to a further refinement of both the list and the criteria, with some compounds dropped and others added.

In applying the criteria to our initial list of compounds little effort was actually made to incorporate human epidemiological information dealing with possible acute toxic effects. This was due primarily to the fact that the main purpose of the regulations for which the list was being developed was to protect against serious adverse effects which might be posed by long term, or chronic exposure to these pollutants.

With regard to exposure, in order to determine whether or not a particular substance is present in industrial effluent discharges, the work group investigated all data sources available to the Agency. Only those compounds for which there was information indicating actual presence in point source effluent, or strong likelihood that the compound is present, were considered candidates for priority consideration. In determining which compounds are present in point source discharges, the work group undertook the following steps.

First, EPA's Effluent Guidelines Division compiled a "direct discharge emissions inventory", which in turn was followed by a "discharge parameter matrix" in which the pollutants known or strongly believed to be discharged were listed by industry, coupled with such information as was available on quantification. The principal sources of the raw data were permits and permit applications, monitoring data, and information gathered by EPA contractors in the course of their developing the required data base to support existing effluent limitations guidelines.

Second, we prepared an "effluent load reduction study", based on a sample of 1800 national pollutant discharge elimination system permits, which list the maximum allowable discharge for various pollutants. An estimate was made of the quantity of each pollutant discharged per day for each of the regulated 43 industrial point source categories. By summing these estimates for each pollutant, a rough estimate of the total discharge for point sources could then be made for many of the pollutants. Even when supplemented by monitoring reports, there are statistical and other limitations on this type of data, and therefore it was used with caution.

In addition, the work group reviewed the several studies mentioned earlier on the presence of many of the selected compounds in surface water as well as drinking and well water.

With respect to food (particularly fish and fish products) and humans, additional monitoring sources were examined. These included specifically the FDA Market Basket Survey and the EPA Human Monitoring Survey, which were notably helpful regarding pesticides and heavy metals.

The prime source for data on annual production was the Stanford Research Economic Handbook, which apparently derives a good deal of its information from Federal Trade Commission data as well as from industry surveys. Relatively little data were obtained on use patterns. For the purposes of this selection process, however, it was less important to know the ultimate use than it was to know the source and amount of the industrial discharge of these compounds.

With respect to the final "exposure" criterion, "analytical methodology capabilities", the work group ascertained that there were and are currently available analytical methods capable of detecting all of the 65 high priority compounds and/or generic categories on our final lists, although the degree of confidence in the analytical methods used to detect these pollutants varies somewhat especially at low concentrations.

The group completed its work in February, 1976. Its final work product was four lists, consisting of 29, 18, 18, and 11 substances respectively. The 29 pollutants on the first list which has the highest priority, meet the following criteria:

A. The pollutants are known to occur in point source effluents, in aquatic environments, in fish, or in drinking water.

B. There is substantial evidence of carcinogenicity, mutagenicity and/or teratogenicity in human epidemiological studies or in animal bioassay systems.

C. It is likely that point source effluents contribute substantially to human hazard, at least locally. This latter judgment is based on consideration of the quantities emitted, the persistence of the compounds in aquatic systems, their tendency to be stored in organisms used for human food, and available information on effective doses in animal tests.

This first list contained the following substances:

LIST 1

1. Acenaphthene
2. Aldrin/Dieldrin
3. Arsenic compounds
4. Asbestos
5. Benzene
6. Benzidine
7. Beryllium compounds
8. Cadmium compounds
9. Carbon tetrachloride
10. Chlordane (technical mixture and metabolites)
11. Chloroalkyl ethers (chloromethyl, chloroethyl, and mixed ethers)
12. Chloroform
13. Chromium compounds
14. DDT and metabolites
15. Dichlorobenzenes (1, 2-, 1, 3-, and 1, 4-dichlorobenzenes)
16. Dichlorobenzidine
17. Diphenylhydrazine
18. Heptachlor and metabolites
19. Hexachlorocyclohexane (all isomers)
20. Lead compounds
21. Mercury compounds
22. Nickel compounds
23. Nitrosamines
24. Polychlorinated biphenyls (PCBs)
25. Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes, and indenopyrenes)
26. 2,3,7,8 - Tetrachlorodibenzo-p-dioxin (TCDD)
27. Thallium compounds
28. Trichloroethylene
29. Vinyl chloride

The 18 pollutants on the second highest priority list satisfy criterion A, above, i.e., occurrence in point source effluents, in aquatic environments, in fish, or drinking water. However, in some cases the evidence of carcinogenicity, mutagenicity, and teratogenicity is based primarily upon structual similarity to compounds in List 1, or upon mutagenic activity in bacterial screening systems; or testing has shown some evidence of carcinogenicity, mutagenicity, or teratogenicity, but these results presently appear to be incomplete or equivocal. In addition, a few compounds are included in List II on the basis of serious toxic effects other than carcinogenicity, mutagenicity, or teratogenicity. These other serious toxic effects are, for the most part, on aquatic organisms. Finally, the possibility of significant human exposure attributable to point source effluents was judged to be somewhat less than that for compounds in List I. (This judgment was based on relatively small volume of discharges, or relatively low propensity to persist in water or to accumulate in organisms.)

The substances on List II are as follows:

LIST II

1. Chlorinated benzenes (other than dichlorobenzenes)
2. Chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane, and hexachloroethane)
3. 2-chlorophenol
4. Dichloroethylenes (1,1-and 1,2-dichloroethylene)
5. 2,4-dichlorophenol
6. 2,4-dimethylphenol
7. Dichloropropane and dichloropropene
8. Endosulfan and metabolites
9. Endrin and metabolites
10. Fluoranthene
11. Haloethers (other than those in List I; includes chlorophenyl ethers, bromophenylphenyl ether, bis(dischloroisopropyl) ether, bis-(chloroethoxy) methane and polychlorinated diphenyl ethers)
12. Halomethanes (other than those in List I; includes methylene chloride, methylbromide, bromoform, dichlorobromomethane, trichlorofluoromethane, dichlorodifluoromethane, methylchloride)
13. Hexachlorobutadiene
14. Naphthalene
15. Pentachlorophenol
16. Phthalate esters
17. Tetrachloroethylene
18. Toxaphene

With respect to the 18 compounds on priority List III, all satisfy criterion A: occurrence in aquatic environments, in fish, or drinking water. In addition, all are known to have toxic effects on human or aquatic organisms at relatively low concentrations. However, there is no substantial evidence that these compounds have primary carcinogenic, mutagenic, or teratogenic effects. List III contains the following compounds:

LIST III

1. Acrolein
2. Acrylonitrile
3. Antimony compounds
4. Chlorinated naphthalene
5. Chlorinated phenols (other than those in List II; including trichlorophenols and chlorinated cresols)
6. Copper compounds
7. Cyanides
8. Dinitrotoluene
9. Ethylbenzene
10. Hexachlorocyclopentadiene
11. Isophorone
12. Nitrobenzene
13. Nitrophenols (including 2,4-dinitrophenol, dinitrocresol)
14. Phenol
15. Selenium compounds
16. Silver compounds
17. Toluene
18. Zinc compounds

The 65 compounds on these 3 lists are receiving the highest priority in the Agency's regulatory programs currently being implemented under the Federal Water Pollution Control Act. They are listed together as Appendix A to the consent decree issued in June, 1976, by the U. S. District Court for the District of Columbia which was mentioned earlier.

In addition to these three lists, the work group developed a fourth list of compounds which is receiving secondary regulatory attention by the Agency. Compounds on this list are also known to occur in effluents or drinking water. On the basis of existing evidence, they are judged to present a less substantial direct hazard than the chemicals on Lists I-III. However, there is reason to believe that they may be converted in the environment into derivatives or breakdown products which may be regarded as precursors of hazardous compounds rather than major hazards in themselves. List IV originally consisted of 11 items, and chlorine has since been added. Under the consent decree, EPA is to gather data on these 12 pollutants. But is not obligated to issue regulations for them. This list is as follows:

4. SELECTION OF 21 INDUSTRIES

For the 43 industrial categories for which EPA has already issued effluent limitations guidelines in connection with the first round of permits directed towards the July 1, 1977, date, considerable data were obtained on which industries were discharging which pollutants, and in what volume. The principal sources of this data include the NPDES permit applications, monitoring reports, "Development Documents" and other surveys and analyses prepared by EPA's contractors in connection with the development of the first group of regulations, sampling and analysis data, and other reports. The staff report of the National Commission on Water Quality was also considered.

The 21 industries which were selected for the primary regulatory effort have all been found to be discharging a substantial number of pollutants on the list of 65, and in most instances the volumes of such discharges are also substantial.

There was nothing magic in the number 21. The Agency did prepare a rough prioritized ranking of the 43 industries, in the order of discharges of number and volume of pollutants. The selection of the top 21 of these industries reflects nothing more sophisticated than hard negotiations between the Agency and the plaintiff environmental groups in the four lawsuits mentioned above. The environmental groups sought a high number to assure maximum coverage. The Agency sought a lower number to preserve maximum flexibility. In fact there is no question but that regulations ought to be developed for these 21 industries. Moreover, to the extent that resources permit, the Agency may well go beyond the 21 industries and develop comparable regulations for other industries as well.

The order in which the industries appear on the Agency's present working list is not the same as the original priority order. The present order reflects to a large degree the availability of contractors and EPA project officers, and similar administrative considerations. This list of industries is set forth below.

LIST IV

1. Acetone
2. n-alkanes (C_{10} - C_{30})
3. Biphenyl
4. Dialkyl ethers
5. Dibenzofuran
6. Diphenyl ether
7. Methylethyl ketone
8. Nitrites
9. Secondary amines
10. Styrene
11. Terpenes
12. Chlorine

INDUSTRIES FOR WHICH REGULATIONS WILL BE DEVELOPED UNDER THE FEDERAL WATER POLLUTION CONTROL ACT TO CONTROL PROBLEM POLLUTANTS

1. Timber Products Processing
2. Steam Electric Power Plants
3. Leather Tanning & Finishing
4. Iron & Steel Manufacturing
5. Petroleum Refining
6. Nonferrous Metals Manufacturing
7. Paving & Roofing Materials
8. Paint & Ink Formulation & Printing
9. Ore Mining & Dressing
10. Coal Mining
11. Organic Chemicals Manufacturing
12. Inorganic Chemicals Manufacturing
13. Textile Mills
14. Plastic & Synthetic Material Manufacturing
15. Pulp & Paperboard Mills
16. Rubber Processing
17. Soap & Detergent Manufacturing
18. Auto & Other Laundries
19. Miscellaneous Chemicals
20. Machinery & Mechanical Products
21. Electroplating

5. SUBSEQUENT REFINEMENT OF LISTS

Each of these lists is subject to refinement, and the consent decree provides the necessary flexibility to do so. Industries or industrial subcategories may be added or deleted. Scientific knowledge never stands still. It may be that as the program is implemented, some substances will be added and others deleted. While great efforts and talents were brought to bear in selecting the original 65, no one suggests that this list is perfect.

It should be noted that some of the items on this list are actually families of compounds. As of this date, in implementing the program, EPA has broken out the families into individual substances, and has further prioritized within these families. This has resulted in a refined working list of 129 substances.

The process by which this further refinement has been accomplished will be discussed next by Walter M. Shackelford of EPA's Athens, Georgia, Laboratory.

This concludes my presentation. I will be glad to answer any questions you may have.

REFERENCES

The author wishes to express appreciation to the Chairman of this task force, John C. Kolojeski, who was formerly with EPA's Office of General Counsel and Office of Water and Hazardous Materials, and is now President of Clement Associates, Inc., scientific regulatory consultants in Washington, D.C., for his assistance in documenting various activities of the task force as discussed in this paper.

BIOGRAPHY

Ridgway M. Hall, Jr. is Associate General Counsel, Water Quality Division, of the Environmental Protection Agency. He is responsible for advising and representing the Agency on all legal matters relating to the quality of the nation's waters, which includes primarily issues arising under the Federal Water Pollution Control Act and the Safe Drinking Water Act. He received his B.A. degree from Yale University in 1963 and his L.L.B. degree in 1966 from Harvard Law School. He is a former partner in the law firm of Cummings and Lockwood of Stamford, Connecticut, where he practiced law from 1966-1975. Mr. Hall is a member of the American Bar Association Sections on Litigation and Natural Resources Law.

DISCUSSION

Richard B. Costa: (CEC Thompson Engineering, Inc. Houston, TX) How many substances on the "list of priority pollutants" are common to both industrial and municipal effluents?

Ridgway Hall: We do have some information in that area but not a lot. We know that a lot of them are coming out of POTW's. The major effort in developing these lists was on direct discharges. We then sought to determine how much of what goes into the public owned treatment works in turn passes through. We have only the roughest kind of data in that area. We know that a number of them do pass through some plants to some degree, but there is still more data gathering to do in that area, and frankly the discharges from the POTW's were of secondary priority to the work group. We will be gathering data in that area as we go about implementing this settlement decree in connection with the development of pretreatment standards. The principal thrust of the pretreatment standards is to require whatever steps are necessary to prevent either upset of the POTW, or pass-through by harmful pollutants in harmful amounts. Where we find these problems, it will indicate to us that those pollutants should be controlled by appropriate pretreatment standards.

Mr. Costa: When would you expect that to be available?

Mr. Hall: It will vary from industry to industry and follow to some extent the schedule which is outlined in the consent decree for the contracts. As you probably know there are five series of dates for the issuance of contracts, the development of proposed regulations, and promulgation. The earlier industries on the administrative timetable will probably see that data start falling out sooner. Most of the contracts have already been let, and people are in the process of gathering data. I would suspect that some of that data will be available in a good deal less than a year and perhaps for some of those early industries as soon as 7 or 8 months from now. The thing to do is contact the project officers on those if you're interested in that kind of data.

A. Karim Ahmed: Will you please explain the list of twelve compounds which you showed on your list No. 4 on the screen? I'm a little unclear about its relation to the implementation of the Consent Decree.

Ridgway Hall: That list survives now as Appendix C to the Settlement Agreement and it's governed specifically under paragraph 4(b) of the Settlement Agreement for those of you who follow those sort of things with a fine tooth comb. Under the Decree, as the Agency goes about its industry-by-industry data-gathering and sampling - analysis efforts, wherever we find any of those 12 compounds present in effluents we will gather data. We will record it so that we will know who is putting out which of the compounds on that list and in what amounts. It will therefore give the Agency a good data base so if we later find out that the compounds are indeed causing problems either through synergistic reactions, or breakdown or metabolite reactions, we'll have the data in hand to go out and promptly develop regulations to deal with those problems rather than having to come back a second time and bother these 21 industries again with another massive data gathering effort.

Peter Foley: The President's message also had a recommendation for changes to Section 307. Could you give us some insight what problems the Agency has with that Section and what amendments they will be seeking?

Ridgway Hall: Yes, I'd be glad to. The principal problem that we have with 307 is the fact that it basically is a pollutant-by-pollutant approach rather than an industry-industry approach. Another problem is that both the standard-setting time frame and the compliance time are very short. But the biggest limitation on its usefulness is that it proceeds on a pollutant-by-pollutant basis. It is inherently disruptive when you are trying to develop a program which will give major coverage to industries for a lot of pollutants. You're trying to regulate and get controls in place for a large number of toxic pollutants. As those of you who are corporate managers and decision makers know, if the Agency can come to you and say, based on data which together we jointly assembled, "The following controls appear sensible and necessary to control everything in your effluent that looks as though it's going to be harmful", you can then go and plan on that. You can buy the technology, you can install it, and you've got a reasonable installation time. You don't have the moving target problem of EPA coming down the road 3 or 6 months later with "Oh, by the way, we just found mercury in your effluent, you've got to put the following technology in for that."

I think the other troublesome features with it are as follows. First, the Agency was told to develop a list of pollutants for regulation under the section within 90 days after passage of the Act. It was then told to develop toxic effluent standards within 180 days after that, and then run formal rulemaking hearings, and within 6 months after proposing the standards to promulgate them. Then industry has only 1 year to comply with those standards. That's a very rigid timetable for the regulatory program in that we have to list the pollutants practically before we go out and gather the data to find out if the pollutants are really troublesome or not. Furthermore, one year is an awfully short time for industry to install meaningful control technology.

I think therefore that the kinds of amendments which you might see are, for one thing, language that would alter the regulatory trigger mechanism by disconnecting the section from 90 days following passage of the Act, which is long since past. While I cannot speak for the Administration at this point, in my personal view the time for listing a pollutant under Section 307(a) should be when information comes to the attention of the Administrator on the basis of which he deems it appropriate to regulate it. This way you gather the data first and then make the regulatory decision. There is also discussion about switching the kind of rulemaking from the formal adversary trial-type proceedings to the more informal rulemaking such as you see under Section 307(b) for pretreatment standards. This would be notice and comment rulemaking with the option of a hearing, if you want it. This was the procedure essentially set out by Congress last year when it passed the Toxic Substances Control Act.

There was a bill which was passed by the House earlier this year which would have allowed some flexibility to extend the one-year compliance time up to three years if the Administrator determines that a further extension beyond the one year is necessary because of technological reasons. That bill died in conference, but I suspect it will come up again. The administration might want to include a provision on that amendment that would direct the Administrator to consider any adverse effects on human health or the environment in determining whether or not to extend the period beyond the one year. One can envision the situation where technology might be installable let's say 2 years down the road but the human health hazard might be so bad you would want to shorten the time notwithstanding the temporary unavailability of technology. Those are the kind of amendments that I would foresee.

EVOLUTION OF THE PRIORITY POLLUTANT LIST FROM THE CONSENT DECREE

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INTRODUCTION

The Consent Decree of 7 June 1976 (1) required the Environmental Protection Agency to assess industrial wastewater with respect to 65 compounds and compound classes. To provide chemical analysis data at a reasonable cost, however, the compound classes listed in the Consent Decree had to be resolved into representative individual compounds. The factors to be considered for such a resolution procedure include the known frequency of occurrence of the compound in water, the number of manufacturing sites and quantity of material manufactured, and the availability of a reference standard. Once the compound classes have been resolved by EPA, generation of a protocol for screening analysis of a variety of effluent types becomes a problem that may be quantified in terms of required analysis procedures such as the number of extractions, instrument runs, etc.

CONSENT DECREE COMPOUNDS

For chemical analysis, the compounds listed in the Consent Decree can be divided into three broad groups. The largest group is composed of those compounds and classes of organic chemicals that are amenable to analysis by gas chromatography-mass spectrometry. Of the 50 listed in this group, 13 are classes of compounds containing as few as two and as many as several hundred known members. The second group consists of 13 metals and their compounds. As with the first group, each of the 13 compound classes in this group could be construed to contain hundreds of constituents. The elements of this group may be analyzed individually by plasma emission spectroscopy, spark source mass spectrometry, or some other method of multielement analysis. The final grouping consists of cyanide and asbestos, two substances that require specialized analysis procedures not applicable to groups of materials.

Obviously, the challenge of chemical analysis of a sample for literally hundreds of components is staggering -- especially when it is considered that these components may be only trace substituents (parts per billion) in the overall sample matrix. The drain on resources in governmental laboratories as well as laboratories in the private sector in terms of manpower and money would be overwhelming if analysis were attempted of effluent samples for the compounds and compound classes of the Consent Decree when construed to their fullest extent. For these reasons it was deemed necessary to resolve the list of 65 Consent Decree compounds and classes into a list of individual compounds that represents faithfully each multicomponent class in the original list of 65. The specific compounds mentioned in the Consent Decree, however, were automatically passed through to the resolved list without further question. In addition, because technology for identification of individual metal compounds, particularly organometallic compounds, is not well developed, the metals were to be analyzed without regard to oxidation state. This segregation of compounds leaves the problem of defining criteria to properly choose representatives of the remaining broad chemical classes.

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CRITERIA USED FOR RESOLVING LIST

To resolve the remaining Consent Decree compounds into a list that presents an analytical problem of finite limits requires that decisions be made that address the spirit and intent of the Consent Decree. For instance, it seems plausible that in deciding which members of a compound class adequately represent the whole class, those compounds that have little chance of finding their way into industrial effluents should be of low priority. Those compounds, however, that are manufactured in quantity, are used in manufacturing processes, or are by-products of other processes would get high priority as group representatives.

Another aspect that may be used to prioritize the compounds that represent a group is the previous occurrence of a given compound in an analysis of water samples. If a candidate for group representation has not been identified in water in some previous study, whereas another candidate has been previously identified, the priority for group representation should be assigned to the latter candidate. The fact that a compound has been identified in water previously is an indication that it is apt to be present in additional similar studies.

A final aspect that must be considered in prioritizing chemical group representatives is the availability of analytical reference standards. Identification and quantification of chemical compounds depends upon the use of reliable standards. If a reliable standard of a candidate compound is not obtainable, quantitative analysis is impossible.

DATA USED IN RESOLVING LIST

The data used to resolve the Consent Decree list of compound classes falls into three sets that are consistent with the above rationales. First, an EPA study of organic compounds identified in water was used to provide the data on the compounds previously detected in surveys of water (2). Second, data concerning the manufacture of compounds was gathered from previously conducted surveys of the chemical industry (3,4). Finally, catalogues from various chemical supply houses were consulted to determine whether analytical standards were available (5-14).

Data previously gathered through analyses of various water types throughout the world provided the most useful basis for identifying the candidates for group representation on the basis of their known existence and known amenability to state-of-the-art analysis techniques. Of the original 65 compounds and classes, 5 had never been detected in water samples. Moreover, 2 of the 13 groups of organics had no representatives that had been previously found in water. In the remaining 11 groups, however, priorities could be set according to the past occurrence of a given group member in water. Table 1 lists the 13 groups and their known frequency of occurrence in water.

Of the individual members of a group that had been found in water previously, those that represented less than 5% of the total occurrence were removed from consideration in the interest of reducing analysis costs. Table 2 shows the 13 groups and the number of compounds that had been found in water within each group. Also listed is the number of compounds within each group that met the greater than 5% occurrence criterion.

Manufacturing data help prioritize candidate compounds as representatives of chemical groups by indicating the amount of a given chemical that the environment may have to absorb. Of the 13 groups of organics that were listed in the Consent Decree, only 9 contained compounds that were manufactured in quantity. Compounds in these 9 groups that had no known manufacturers were given lower priority than those for which production data existed. Table 3 lists the 13 groups of compounds and the number of compounds for which production data existed. The production data overlapped with the frequency data in most cases except that two chlorinated naphthalenes and one nitrosamine are produced but have never been found in water. N-nitrosodiphenyl amine, the rubber chemical, and 2-chloronaphthalene were added to the list on the basis of production. The other materials had already been included because they met the frequency criterion.

The availability of analytical reference standards for the candidate compounds was determined by searching chemical supplier catalogues. As expected, standards for most of the compounds that are manufactured or have been found in water previously were readily available from a number of chemical supply houses. Where possible, noncommercial sources were found for compounds mentioned specifically in the Consent Decree. Those compounds that were only candidates for group representation, however, were dropped from consideration. Table 4 lists the 13 groups and the total number of considered candidates in each group along with the number eliminated because of lack of a standard.

GENERATION OF AN ANALYTICAL PROTOCOL

The reason for resolving the Consent Decree list was to make possible the analysis of industrial effluents for these compounds and classes of compounds within the constraints of available time and money. EPA's Environmental Monitoring and Support Laboratory in Cincinnati was given the responsibility of developing an analysis protrocol for screening the effluents for the compounds on the resolved Priority Pollutant List. The

Athens Environmental Research Laboratory was asked to provide input for the screening analysis protocol for those organic compounds not amenable to the purge and trap (Bellar-Lichtenberg) technique. Once the Priority Pollutant List had been evolved, establishment of the analysis protocol for screening became a problem of applying known methods and techniques to the specific set of compounds on the Priority Pollutant List.

In this case, the development of an analysis protocol also involves the consideration of two aspects that are many times not considered in survey analysis. First, since the actual laboratory work is more than any one contractor could handle, provisions must be made to insure the compatibility of data from one laboratory to the next. Second, this protocol must be limited to looking for only the priority pollutants. The method used (computerized GC-MS), however, would also see--were there time to interpret the data--some of those compounds eliminated as class representatives and others that at some later date may be of interest.

Even though it is recognized that each effluent will present its own set of unique problems, the protocol provides a measure of compatibility by giving a general approach to follow and specifying techniques within the general approach. For instance, gas chromatographic column packing materials are specified and a common lot is to be used by all laboratories involved in the screening analysis.

To save data that will allow the future determination of compounds not on the Priority Pollutant List involves two factors. First, the analysis protrocol must be general enough to allow the detection of compounds other than those on the list. This requirement is satisfied by using extraction, concentration and detection techniques that do not discriminate against any compounds that can be gas chromatographed--essentially state-of-the-art survey analysis with mass spectrometric detection. Second, a method must be developed for long-term storage of the raw data. This requirement is satisfied by coupling a computer system directly to the mass spectrometer so that raw data may be transferred to magnetic tape.

CONCLUSIONS

In listing classes of compounds rather than specific compounds, the Consent Decree presented a problem that to the analytical chemist seemed without practical limit. By using available data concerning previous detection in water, manufactured quantities, and availability of standards, however, the ambiguous compound classes can be replaced with specific compounds of high priority. Once the specific compound list has been resolved, however, the necessity for interlaboratory comparability of data and effective ways to save all raw data becomes even more acute in the development of the final protocol.

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DISCUSSION

J. D. Hallett, Shell Oil Co.: I have two questions. I have heard the words "screening analysis" used several times both by you and Mr. Hall. Can you define this term and would you describe your efforts on the "lab-to-lab" comparability program?

W. M. Shackelford: Screening analysis as intended in the analysis protocol is the qualitative and semi-quantitative analysis of effluents for the 129 priority pollutants. This differs from a survey analysis in that a survey would be concerned with all components in a sample.

J. D. Hallett: Define semi-quantitative.

W. M. Shackelford: Semi-quantitative as we mean it here is quantification by a method that has not been standardized--in this case mass spectrometry.

J. D. Hallett: Are you talking about orders of magnitude?

W. M. Shackelford: As indicated in the protocol, concentration values are to be reported in ranges--10-100 parts per billion (ppb) and greater than 100 ppb. To answer your second question, the program to establish some measure of lab to lab comparability includes supplying contractors with the same lots of GC column packings, analytical standards, and requiring that all data be saved on 9-track magnetic tape in a specified format.

J. D. Hallett: Will the analytical standards be available to industrial labs?

W. M. Shackelford: As far as I know, they will be available commercially.

Don Rosebrook, Radian Corp.: Radian Corporation is the EPA contractor for preparation of the Consent Decree standards. When this order is filled, the standards will be made available to the general public.

Leo Duffy, Standard Oil Co. of Indiana: Many analytical chemists regard the GC-MS to be a totally qualitative instrument. Would you remark on how one establishes a limit of detection with a qualitative GC-MS instrument? Doesn't this limit of detection float and depend on instrument response?

W. M. Shackelford: The term limit of detection as used in the analysis protocol is misleading. Actually, the numbers referred to as limits of detection are required concentrations that must be detected. The 40 ng figure that is given was derived from the amount of material injected after the standard extraction and concentration procedure was performed on a 10 ppb solution. For some compounds the figure is 200 ng. So these are practical working levels--not actually limits of detection. I agree that the mass spectrometer is not quantitative by present methods. However, with the use of our internal standard, d_{10} anthracene, and calculation of response factors for each compound, mass spectrometry appears adequate to establish the ranges of concentrations we have proscribed.

Leo Duffy: In the semi-volatile compounds you list three key fragment ions along with the GC retention time of the compound. Would you remark on the certainty of identification of specific compounds, restricting yourself only to those three key fragment ions?

W. M. Shackelford: If the GC retention time is considered, the confidence in identification by three fragment ions is increased. A window of ± 1 minute, which corresponds to about 10 MS scans on each side of the peak, has proved to be adequate. Of course, identification with absolute certainty can only occur if a standard and unknown are run and the complete spectra compared. For the purposes of the protocol, however, the present method is sufficient.

F. L. Robertaccio, E. I. DuPont de Nemours Inc.: How much of your experience has been on applying these methods to complex wastewaters?

W. M. Shackelford: The analysis protocol essentially involved the use of techniques used at the Athens laboratory for the past three to five years. The Analytical Chemistry Branch has been concerned with characterization of effluents and essentially all of our experience has been using methods similar to those in the protocol. Although some work has been done on drinking water, much has been done with actual effluents. The analysis protocol has also been run on effluents in our lab.

N. F. Seppi, Marathon Oil Co.: You mentioned chlorination of waters. Would you elaborate on whether or not this affects the concentration of chlorinated compounds found in water?

W. M. Shackelford: The only elaboration I can make is to quote papers and reports that indicate that after chlorination of water containing organic materials occurs, chlorinated organics are found. Whether or not increases in the concentration of chlorinated compounds present before chlorination occurred, I do not know. Studies have shown that chlorinated compounds not found before chlorination do show up after chlorination.

BIOGRAPHIES

Walter M. Shackelford

Walter M. Shackelford is a Research Chemist in the Analytical Chemistry Branch of EPA's Athens Environmental Research Laboratory. He has a B.S. degree in Chemistry from the University of Mississippi and a Ph.D. degree in Analytical Chemistry from Georgia Tech. Prior to his work with EPA, Dr. Shackelford was a post-doctoral research associate with G.G. Guilbault at the University of New Orleans and spent two years in research for the U.S. Army at Edgewood Arsenal, Md.

Lawrence H. Keith

Lawrence H. Keith received his Ph.D. from the University of Georgia in 1966. He worked at the Athens Environmental Research Laboratory in Athens, Georgia for over 10 years under the U. S. EPA and its predecessors. Dr. Keith is the editor of the book, Identification and Analysis of Organic Pollutants in Water, and author or co-author of 39 technical publications including 10 chapters in five books. At Radian Corporation he is Head of the Organic Chemistry Department and is responsible for the direction of a technical staff of 24. He is the Secretary of the ACS Division of Environmental Chemistry, Chairman of the Division Steering Committee for the North American Council on Organic Pollutants (NACOP), and Vice-Chairman of the next Gordon Research Conference on Environmental Sciences: Water.

TABLE 1 TOTAL FREQUENCY OF OCCURRENCE FOR 13 CHEMICAL GROUPS

Consent Decree Group	Number of Observations*
Chlorinated Benzenes	247
Chlorinated Ethanes	138
Chloroalkyl Ethers	67
Chlorinated Naphthalenes	0
Chlorinated Phenols	92
Dinitrotoluenes	14
Haloethers (other than above)	15
Halomethanes	360
Nitrophenols	13
Nitrosamines	0
Phthalate Esters	183
Polynuclear Aromatic Hydrocarbons	49
DDT Metabolites	23

*5700 Total Observations for Study

TABLE 2 FREQUENCY OF PRIOR OCCURRENCE OF COMPOUNDS WITHIN 13 CHEMICAL GROUPS

Consent Decree Group	Number of Compounds	Number of Compounds Meeting 5% Criterion
Chlorinated Benzenes	28	9
Chlorinated Ethanes	19	9
Chloroalkyl Ethers	15	4
Chlorinated Naphthalenes	0	-
Chlorinated Phenols	16	5
Dinitrotoluenes	4	4
Haloethers (other than above)	4	4
Halomethanes	17	9
Nitrophenols	4	4
Nitrosamines	0	-
Phthalate Esters	19	7
Polynuclear Aromatic Hydrocarbons	12	9
DDT Metabolites	2	2

TABLE 3 MANUFACTURING DATA FOR 13 CHEMICAL GROUPS

Consent Decree Group	Number of Compounds With Production Data
Chlorinated Benzenes	4
Chlorinated Ethanes	5
Chloroalkyl Ethers	0
Chlorinated Naphthalenes	2
Chlorinated Phenols	3
Dinitrotoluenes	2
Haloethers (other than above)	0
Halomethanes	4
Nitrophenols	4
Nitrosamines	1
Phthalate Esters	2
Polynuclear Aromatic Hydrocarbons	0
DDT Metabolites	0

TABLE 4 NUMBER OF COMPOUNDS ELIMINATED DUE TO LACK OF ANALYTICAL STANDARDS

Consent Decree Group	Number of Considered Compounds	Number of Compounds Eliminated
Chlorinated Benzenes	9	2
Chlorinated Ethanes	9	2
Chloroalkyl Ethers	8	2
Chlorinated Naphthalenes	2	0
Chlorinated Phenols	6	0
Dinitrotoluenes	4	1
Halothers (other than above)	4	1
Halomethanes	10	0
Nitrophenols	6	0
Nitrosamines	3	0
Phthalate Esters	7	2
Polynuclear Aromatic Hydrocarbons	9	2
DDT Metabolites	2	0

"INCORPORATION OF THE PRIORITY POLLUTANTS INTO EFFLUENT GUIDELINES DIVISION DOCUMENTS"

Robert W. Dellinger
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The purpose of this paper is to explain the role of the Effluent Guidelines Division relative to the 1976 Settlement Agreement (1). It will also provide some incite into the overall relationship between the Effluent Guidelines Division and other responsible offices regarding future regulations which will be affected by the Settlement Agreement.

BACKGROUND

The Effluent Guidelines Division (EGD) is a division of the Office of Water Planning and Standards within the Office of Water and Hazardous Materials. The EGD was founded in August of 1972 with the primary function of contributing to the establishment of effluent limitations and guidelines and standards of performance for new sources pursuant to Sections 301, 304, and 306 of the Federal Water Pollution Control Act as amended in 1972. This Act is commonly referred to as Public Law 92-500. The division was originally headed by Allen Cywin and is now headed by Robert Schaffer. Over the past several years, the EGD has been involved in the publication of some 1700 regulations covering over 250 subcategories within 43 industrial point source categories.

As of June 7, 1976, the function of the EGD has taken a new slant. On June 7, 1976, the Settlement Agreement with the Natural Resources Defense Council, et al., came into effect and settled several cases in the District Court for the District of Columbia (1). This Settlement Agreement requires that EPA give consideration to 65 specific chemicals or classes of chemicals when establishing effluent limitations reflecting the best available technology economically achievable, also referred to as BAT or 1983 limitations. This requirement for consideration of the list of chemicals carries over to the establishment of New Source Performance Standards and to the establishment of pretreatment standards for new and for existing sources. The authority by which EPA has been directed to perform this task derives from Sections 301, 304 (b), 306, 307 (b), and 307 (c) of Public Law 92-500 (2). The Settlement Agreement also establishes a schedule within which contracts are to be let, regulations proposed, and regulations promulgated for a prioritized list of 21 industrial categories.

PRELIMINARY EFFORTS

Several activities had to be completed before the role of the Effluent Guidelines Division relative to the Settlement Agreement could be definitized. These activities included further work with the list of 65 chemicals or classes of chemicals, development of sampling and analysis procedures, and the letting of contracts in order that work could begin on a timely schedule.

In order to enable the Agency to conduct a proper scientific study of industrial discharges, the various pollutant parameters were further defined. Without this information as a point of reference, the analytical portion of the BAT review would be unmanageable given the limited time schedules and resources of the Agency. This list of 65 chemicals or classes of chemicals was defined in November of 1976 to include 123 specific unambiguous compounds. This list of 123 specific compounds appeared in Portfolio B of the Petroleum Refining Industry Survey distributed to the industry in February of 1977. Since that time, the list has been revised. This occurred in April of 1977 with the addition of 6 compounds; now the priority pollutant list totals 129 compounds (3). The six additional compounds include 5 additional PCB's and di-n-octyl phthalate. We believe that this list fulfills the requirements of the court approved agreement and can be evaluated analytically.

In addition, the Agency has established procedures for sampling and analysis of industrial effluents for the priority pollutants. These procedures are defined in the "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants" published in March of 1977 and revised in April of 1977 (4).

While these tasks were being completed by personnel within various program areas of EPA, the Effluent Guidelines Division set about to fulfill its requirements relative to the Settlement Agreement. Due to a relatively small staff, the EGD has historically depended on outside contractors to aid in the fulfillment of its tasks. EGD technical personnel serve as project officers. Their function is to monitor, assist, direct, and provide various inputs to the contractor. The project officer works directly with the contracting firm, usually on a daily basis. One of his main duties is to provide the contractor with information regarding EPA policy.

The Effluent Guidelines Division should meet the schedule for executing contracts that was established in the Settlement Agreement. The EGD let ten contracts prior to January 1, 1977 (These included the timber products, steam and electric, leather tanning, iron and steel, petroleum, paint and ink, coal mining, ore mining, nonferrous metals, and paving and roofing industries.). In addition, contractors have been selected for ten of the remaining eleven industrial categories and negotiations are currently going on between the selected contracting firms and EPA procurement. The miscellaneous chemicals request for proposal will be readvertized and will involve multiple awards rather than a single award. Six of the eleven contracts are scheduled for award by June 30, 1977. The additional five will be awarded by October 31, 1977. The Scope of Work to be fulfilled by each of the contracting firms is defined in "Request for Proposal No. WA 77-B074" dated February 7, 1977 (5). The contractor currently involved in the petroleum refining industry study is Burns and Roe of Paramus, N.J. EPA personnel from the Robert S. Kerr Environmental Research Laboratory (RSKERL) are participating in the sampling and analysis phase of the study. Another contracting firm, Ryckman, Edgerley, Tomlinson & Assoc., Inc. (RETA) of St. Louis, Missouri, is also assisting in sampling and analysis.

DUTIES OF THE EFFLUENT GUIDELINES DIVISION

The Effluent Guidelines Division with the help of contractors will perform the function of gathering and analyzing data. Its tasks include the determination of presence or absence of the priority pollutants within waste water generated by industrial point source categories or subcategories, an evaluation of the quantities of priority pollutants present in these waste waters, a determination of the extent to which these priority pollutants exist subsequent to treatment by various control technologies, and an estimate of the cost of implementing these various control and treatment technologies. This information will be used during the decision-making processes established within the Agency in fulfilling the requirements of the Settlement Agreement.

The first step involved in completion of these tasks involves the development of a profile of the industrial point source category. This involves an identification of the plants which comprise the point source category in terms of size, location, and number. It also includes a determination of such information as the numbers of direct versus indirect dischargers, an identification of the treatment systems employed at each plant, both end-of-pipe and in-plant, and an identification of products produced or unit operations employed at plants in the industry. This information forms the foundation on which other information is based and will be usually obtained by submission of a questionnaire to all or a statistically representative portion of the industry. Portfolio A of the Petroleum Refining Industry Survey provides the Agency the means to profile the petroleum refining industry.

An important part of the study is the determination of presence or absence of the priority pollutants. This will be accomplished in part by literature searches, but the major thrust of this exercise involves the implementation of a sampling program. Presence or absence will be determined by a "screening study" (4). This screening study involves the gathering of raw water, raw waste water, and final treated effluent samples for analyses for the priority pollutants. Analyses involve gas chromatography/mass spectrometry (GC/MS) techniques for volatile and semi-volatile organics as well as analysis for metals and pesticides (4). Upon obtaining the results of this screening survey, decisions will be made regarding the necessity to further investigate certain of the priority pollutants. These decisions will be based on the guidance provided in paragraph 8 of the Settlement Agreement (1). Exclusion of parameters can be justified if the specific pollutant is present soley as a result of its presence in intake waters, or if the specific pollutant is either not present in the discharge or is present in insignificant quantities and not likely to cause toxic effects.

Upon making the decision of which parameters to be concerned with relative to a point source category or subcategory, the second phase of the sampling program is implemented. This involves verification or quantification of the amount of priority pollutants present. It also, ideally, involves a determination of the unit operation or operations which result in the discharge of the specific priority pollutants of concern. In the quantification phase the degree to which the priority pollutant is removed by various existing treatment systems within the point source category will be evaluated.

As more of these BAT studies get underway and data become available, the potential exists for supplementing information relative to one point source category with data from another point source category. This could involve a transfer of technology from a point source category where a more advanced technology is practiced to one in which a lesser technology is practiced. It is very early in the program to predict to what degree, if any, direct transfer of technology could or would be applicable or whether or not it is, in fact, necessary or desirable.

The EGD will also develop cost data to correspond to the various technologies thought to be potential BAT technologies. This may include in-plant control measures, recycling techniques to reduce wastewaster discharges, source control prior to biological treatment, or end-of-pipe technologies. Efforts will be made to provide good capital and operating cost estimates for the identified potential BAT technologies.

EGD Efforts to Date Relative to the Petroleum Refining Industry

Regarding the petroleum refining industry specifically, this overall EGD work plan has been altered slightly. Due to time constraints and delays, a decision was made to combine the screening and quantification phases into a single program. Initially, twelve plants were to be sampled. At six of the plants, pilot activated carbon studies will be conducted. This sampling study is now being conducted by RSKERL. A rationale was developed for selection of twelve individual refineries to be sampled (6). This involved establishing the following criteria for selection:

1. The selected plants must be BPT plants; i.e., they must be attaining BPT limitations or fulfilling the requirements of their July 1, 1977, permit requirements.

2. The selected plants would have a single outfall. This criteria was established strictly due to economic considerations, namely the large cost of analysis of individual samples.

3. The selected plants would cover as many of the unit operations found in the petroleum refining industry as possible, and

4. The selected plants would represent various crude sources. Because no completed questionnaires had been received at the time of selection, it was agreed that this criteria would be met through a selection of plants with a wide geographic distribution.

A secondary consideration was that in the selection of the six refineries where pilot carbon studies would be performed, at least four would involve activated sludge treatment. The other two would also involve some other form of biological treatment (i.e., aerated lagoons, oxidation ponds, etc.).

The EPA contractor, Burns and Roe, went to work on developing the list of 12 refineries to be sampled. They visited EPA regional offices and State offices. They gathered Discharge Monitoring Report data while speaking to Regional and State personnel. Forty five refineries were identified which met the first two criteria (attainment of BPT limitations while having a single outfall) (6). The Oil and Gas Journal was searched to determine the unit operations employed at the various refineries. The fourth criteria of geographic mix was added to the selection process.

A matrix was developed which resulted in the compilation of a list of 12 refineries to be sampled with 2 alternates corresponding to each selected refinery. The current petroleum refining industry sampling study is based on this list of 36 plants.

Various contacts were made with the American Petroleum Institute and the National Petroleum Refiners' Assocation to inform them of the refineries selected for sampling. API representatives contacted individual plants to determine the mode of operation for the duration of the sampling study, March to July. Based on this additional information, several first choices dropped out due to various reasons (such as scheduled turnarounds and strikes). Representatives of alternate refineries were contacted. A sampling schedule was then developed around the availability of the selected refineries. The decision was made that due to the time constraints imposed by the Court and due to the tremendous workload on RSKERL personnel, this sampling schedule would be strictly adhered to.

With the unavailability of certain refineries and a shift to alternates, the final list of 12 refineries to be sampled omitted several unit operations. Additional funding became available relative to the petroleum refining industry study. The decision was made to supplement the initial sampling program by sampling additional plants. Ryckman, Edgerley, Tomlinson, and Associates, Inc. is conducting the supplemental sampling program which, at the present time, includes 5 refineries (7). Table I gives a listing of the petroleum refineries to be sampled in the BAT review and the scheduled date of initiation of the sampling program at each individual refinery.

THE RELATIONSHIP OF RESPONSIBLE PROGRAM AREAS

The total of the information gathered by the Effluent Guidelines Division forms a part of the technical information on which final effluent limitations will be established. Other studies are being conducted by other divisions within the Office of Water Planning and Standards. Major inputs will be made by the Criteria and Standards Division headed by Dr. Kenneth Mackenthun, by the Monitoring and Data Support Division headed by Dr. Edmund M. Notzen, and by the Office of Analysis and Evaluation headed by Mr. Swep Davis.

The Criteria and Standards Division (CSD) is responsible for studies relating to health and environmental effects, will provide physical and background data relating to the priority pollutants, and will interface with other government agencies to obtain health and environmental effects information.

They will also develop specific criteria that will provide justification for regulation of the priority pollutants.

The Monitoring and Data Support Division (MDSD) is responsible for general studies of each priority pollutant including geographical and quantitative profiles of users and manufacturers, and for a summary of losses of priority pollutants to the environment through discharges to water by industrial producers and users, municipalities, agricultural sources, and natural sources. They will develop a data base associated with each industrial category and gather information relating to ambient water quality to provide an overview of the magnitude and geographical extent of potential problem areas. This information will be used to provide an overall risk assessment based on the quantity of priority pollutants released and their environmental effects.

The Office of Analysis and Evaluation (OA&E) is responsible for economic impact studies which will include an increased emphasis toward benefit analysis. Economic studies will include a clear description and evaluation of load reductions, of health and water quality risk avoidance, and of correlations between industry location, water quality, and potential health problems.

The inputs of all responsible program areas merge at the working group level. Working groups involve personnel representing the responsible program areas but include personnel representing such groups as Research and Development, Toxic Substances, Pesticide Programs, Air Programs, General Counsel, Enforcement, Planning and Evaluation, and EPA Regional Offices. Decision-making will begin at the Working Group level with recommendations regarding regulations passed along to EPA management for evaluation.

At the present time, working group activity relative to the petroleum refining study has been limited to plant selection for the sampling program and other inputs relating to the technical (EGD) and economic (OA & E) studies. As more information is collected, the Working Group will take a more active role in the decision-making process.

MAJOR MILESTONES

The following is a schedule of the major milestones which are important relative to the petroleum refining BAT study:

EPA Draft Development Document Available for Public Comment - March 7, 1978.

Public Meeting to Discuss Draft Development Document - April 7, 1978.

Proposal of Regulations in the Federal Register - July 15, 1978.

Public Meeting to Discuss Proposed Regulations - September 22, 1978.

Promulgation of Regulations in the Federal Register - January, 22, 1979.

SUMMARY

The Agency has a considerable amount of work to do relative to the Settlement Agreement. The EGD has a major area of responsibility, that of gathering the technical information on which standards will be established. The petroleum refining study is in the early stages of development; we are awaiting the results of GC/MS analysis for non-volatile organics and the results of metals and pesticides analyses. Upon receipt of this data, the Agency will make the decisions, at the working group level, which will determine the immediate direction which the petroleum refining study will take.

REFERENCES

(1) Natural Resources Defense Council, et al. v. Train, 8 E.R.C. 2120 (D.D.C. 1976).

(2) Public Law 92-500, 92nd Congress, S. 2770, October 18, 1972.

(3) "Rationale for the Development of BAT Priority Pollutant Parameters," Effluent Guidelines Division, Office of Water and Hazardous Materials, U.S. Environmental Protection Agency, Washington, D.C., June, 1977.

(4) "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, April, 1977.

(5) "Request for Proposal No. WA 77-B074," U.S. Environmental Protection Agency, Washington, D.C., February 7, 1977.

(6) "Selection of Refineries for RSKERL Sampling Program," Burns and Roe Industrial Services Corporation, Paramus, NJ, February 22, 1977.

(7) "Selection of Refineries for B&R Supplemental Sampling Program," Burns and Roe Industrial Services Corporation, Paramus, NJ, May 4, 1977.

DISCUSSION

Paul Mikolaj, Lion Oil Co.: When will the results of EPA's preliminary screening studies be available?

R. W. Dellinger: As of next week, 14 of the 17 plants which have been scheduled for sampling will have been visited. Results of the first 6 refineries screen-sampled by RSKERL are anticipated to be received by EGD around mid-June. It was originally anticipated that this data would be received by the end of May. Data relating to the other refineries sampled by RSKERL and RETA will be available at a much later date. It is too early to predict the actual date of availability at this time; we are pretty much at the mercy of the analytical labs with regard to turnaround time.

Paul Mikolaj: Will this information be publicly available?

R. W. Dellinger: Eventually this information will be publicly available and published in an EPA development document. Between now and that time, I would anticipate that there will be an exchange of data between EPA and representatives of the individual refineries where split samples were taken. In any event, the EPA data will be submitted to the refineries as soon as data become available.

BIOGRAPHY

Robert W. Dellinger is a chemical engineer with the Effluent Guidelines Division of EPA. He has B.S. and M.S. degrees in Chemical Engineering from Virginia Polytechnic Institute and the University of Maryland, respectively. He has been with the Effluent Guidelines Division since November of 1972.

TABLE I

PETROLEUM REFINERIES SCHEDULED FOR SAMPLING AS OF JUNE 3, 1977

Refinery	Location	Scheduled Date	Carbon?	Group Conducting Sampling (1)
Gulf	Philadelphia, PA	3/21	No	RSKERL
Exxon	Baytown, TX	3/21	No	RSKERL
Clark	Hartford, IL	3/28	No	RSKERL
Hunt	Tuscaloosa, AL	3/28	No	RSKERL
Texaco	Lockport, IL	4/4	No	RSKERL
Mobil	Augusta, KS	4/4	No	RSKERL
Getty	El Dorado, KA	4/18	No	RETA
Phillips	Sweeny, TX	5/2	Yes	RSKERL
Shell	Anacortes, WA	5/2	Yes	RSKERL
Conoco	Ponca City, OK	5/16	No	RETA
Asamera	Commerce City, CO	5/23	No	RETA
Exxon	Billings, MT	5/30	Yes	RSKERL
Exxon	Benicia, CA	5/30	Yes	RSKERL
Quaker State	Newell, WV	6/6	No	RETA
Sun	Toledo, OH	6/13	No	RETA
Coastal States	Corpus Christi, TX	6/27	Yes	RSKERL
Arco	Philadelphia, PA	6/27	Yes	RSKERL

(1) All sampling teams are assisted by Burns & Roe of Paramus, NJ

GENERATING DATA ON THE PRIORITY POLLUTANTS FOR THE EFFLUENT GUIDELINES DIVISION

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Source Management Branch
Robert S. Kerr Environmental Research Laboratory
Ada, Oklahoma

During the past decade, the Citizens of the United States have become vitally interested and involved with the environmental conditions of the Nation's water supplies. Our Congressional leaders recognized this concern, and in October 1972, enacted legislation "to restore and maintain the chemical, physical, and biological integrity of the Nation's waters."[1]

Within the framework of the Federal Water Pollution Control Act Amendments of 1972, the newly created Environmental Protection Agency was directed, as National Policy, to prohibit the discharge of toxic pollutants in toxic amounts (Section 101.(a) (3). Also, in Section 101 of PL 92-500, sub-section (a) (6) declares that "it is the National Policy that a major research and demonstration effort be made to develop technology necessary to eliminate the discharge of pollutants into the navigable waters of the contiguous zone and the ocean."

Section 307 (a) of the act requires EPA to publish a list of toxic pollutants and to promulgate effluent standards for such toxic pollutants. The following characteristics shall be taken into account; "the toxicity of the pollutant, its persistance, degradability, the usual or potential presence of the affected organisms, and the nature and extent of the effect of the toxic pollutant on such organisms."

In September 1973, EPA promulgated a list of nine toxic pollutants and in December 1973, proposed standards for these nine toxic pollutants.

On June 7, 1976, a settlement agreement was signed between Russell Train, EPA Administrator, and four concerned citizen organizations to investigate the presence of 65 parent chemical constituents reported to be present in the Nation's water supplies. The 65 chemicals are listed in Table 1. This settlement agreement also listed 21 point source categories by Standard Industrial Classification (SIC)including 2911 Petroleum Refining.

After the agreement was signed, the EPA's Effluent Guidelines Division was delegated the responsibility to satisfy the legal conditions of the document. After preliminary meetings regarding the sampling, analytical, and data storage protocols related to the study, the Robert S. Kerr Environmental Research Laboratory (RSKERL) in Ada, Oklahoma, was contacted to provide technical assistance in sampling and analysis for the petroleum refining industry.

A meeting was held in Ada in November with representatives of EPA's Effluent Guidelines Division, the Office of Research and Development, an

American Petroleum Institute Task Force, and key RSKERL personnel. The meeting provided an insight regarding potential sampling and analytical problems associated with the general protocols presented by Effluent Guidelines Division's Quality Control Branch.

From the results of this meeting, a preliminary plan was proposed and accepted. Phase I was designed as a screening study to determine the presence or absence of the priority pollutants, and Phase II was a screening carbon study. Sampling and analytical procedures presented two major problem areas which needed immediate attention; these problem areas were:

Sampling: The original protocol dated November 1976, required automatic samplers be used to collect composite samples. Most automatic samplers use petroleum-derived tubing which has the ability to adsorb or desorb organics from the tubing walls into the water sample. Another problem in using automatic samplers is the lack of electrical safety devices required when sampling in an explosive atmosphere area such as the API separator. A variance was requested to allow the sampling be conducted by EPA personnel; this was granted due to the aforementioned problems.

Analytical

The list of 65 chemical compounds, presented problems to the analysts because of the ambiguity and colossal analytical effort in separating, identifying, and quantifying most of the compounds, metabolites, and isomers which appeared on the list. A list of "Unambiguous Compounds" was prepared to specifically name each pollutant which is to be identified.

This list was prepared by scientists from EPA's Athens, Georgia, laboratory and personnel of the Effluent Guidelines Division. The list of unambiguous compounds was derived from a compendium of information gathered by these scientists from an earlier study on organic compounds in potable water supplies. The list of compounds shown in Table 2 is identical to the specific compounds listed in the settlement agreement. The classes of compounds are represented by carefully selected individual material. The EPA list was discussed with the plaintiffs of the settlement agreement, and there was no dissension.

Another analytical problem encountered was the protocol prepared in November by EPA scientists from the Cincinnati and Athens Laboratories The November protocol was a preliminary analytical exercise and was distributed for review comments by industrial, society, and EPA scientists. In November, a meeting was held at Atlanta, Georgia, with EPA participants from Effluent Guidelines, Athens, and Ada. A request was made to prepare a specific protocol for non-volatile organics and volatile organics analytical procedure. Athens scientists prepared the protocol for non-volatile organics, and Cincinnati scientists prepared the protocol for the volatile organic compounds. The procedures were merged into one protocol and presented in March 1977. These were the major problems encountered in making preparations for this study, and they were corrected prior to the study date.

In November, RSKERL requested a list of 12 refineries be selected by Effluent Guidelines for the field study. The selected refineries would be representative of the five refinery categories, various crude oil sources, geographic locations, and meet Best Practicable Control Technology Currently Available (BPCTC), or EPA regional permit conditions. An alternate list of six refineries meeting the aforementioned conditions was to be furnished in the event that one or more of the primary selections become unavailable.

Effluent Guidelines would then contact the American Petroleum Institute who would contact the refinery to determine if there were any planned turnarounds or other problems which could interfere with the purpose of the study. After the selected refineries had been contacted by API and the results relayed to Effluent Guidelines, a final selection of refineries was prepared. After confirming the selected refineries, the Effluent Guidelines' Project Officer notified each refinery they would be visited by the RSKERL team for the priority pollutant study. The 12 refineries to be visited by RSKERL personnel for sampling are shown in Table 3.

This study was divided into two phases: Phase I is considered a screening study to determine the presence or absence of priority pollutants, and Phase II is a screening study on the effectiveness of carbon treatment to remove the priority pollutants. These two phases will be discussed separately.

Phase I

Six refineries were selected for this phase, and those refineries were:

1. Gulf, Philadelphia
2. Exxon, Baytown
3. Hunt, Tuscaloosa
4. Clark, Hartford
5. Texaco, Lockport
6. Mobil, Augusta

At each refinery, a minimum of three points were selected for sampling. The intake water to the refinery was selected to provide information on the background quality as related to the priority pollutants. The second sampling point represented the API separator or dissolved air flotation effluent, which would indicate the quality of water that would be expected without biological treatment. The third sampling point selected was representative of the NPDES sampling point; this sampling point represented biologically treated wastewater.

Sampling times were established over a three-day study period, and the composite samples were prepared from aliquots obtained at three-hour intervals. On the first sampling day, the composite sampling began at hour 1300 and was completed at hour 1000, the following morning. Twenty-four hour composite sampling was started at 1200 on the second day and 1100 on the third day and completed at 0900 and 0800, respectively. Grab samples were obtained at the final sampling time for each day. Table 4 indicates the parameter, type of samples, and preservative used for the samples. In addition to the priority pollutant samples, Effluent Guidelines contracted with Ryckman, Edgerly, Thomlinson, and Associates Laboratory to furnish containers and analysis for "classical parameters" for each sampling point. Table 6 is a list of the "classical parameters," type of sample, container, and preservative furnished by the contract laboratory. Equipment used to sample the water was glass, stainless steel, or aluminum to prevent sample contamination.

Figure 1 is a photograph of the screen at the Gulf-Philadelphia Refinery, where their intake water is obtained from the Schuylkill River. Figure 2 is representative of the intake water, this particular sample point is the discharge side of the pump at the Gulf-Philadelphia Refinery. Figure 3 is a photograph of the corrugated plate interceptor used at Hunt Oil in Tuscaloosa, Alabama; this sampling point is also shown in Figure 4 which is a bypass line to the pH meter. Figure 5 is a photograph of the DAF unit the Hunt Refinery uses for a final clarifier; and Figure 6 is the sampling point which is prior to the holding pond.

The six refineries selected for "screening only" have been visited and sampled. At this point in time, a draft has been prepared to describe the refinery's wastewater treatment system, and analyses have been concluded and recorded for the parameters with the exception of volatile organics and nonvolatile organics.

The American Petroleum Institute contracted with Exxon Research to accompany the EPA sampling team and obtain "replicate samples" at Exxon-Baytown. In addition, Gulf-Philadelphia; Texaco-Lockport; Mobil-Augusta; and Exxon - Baytown provided company personnel to accompany the EPA team to obtain replicate samples. A request has been made to each refinery which obtained "replicate samples" to furnish their data for inclusion in the report.

Activated Carbon Screening Study

EPA's Effluent Guidelines Division also selected six petroleum refineries for activated carbon pilot scale screening studies. The petroleum refineries selected are:

	COMPANY	LOCATION	CLASS	TREATMENT SYSTEM
1.	Shell	Anacortes, Wash.	B	activated sludge
2.	Phillips	Sweeney, Tex.	C	aerated lagoon
3.	Exxon	Benecia, Cal.	B	activated sludge
4.	Exxon	Billings, Mont.	C	aerated lagoon
5.	Coastal States	Corpus Christi, Tex.	C	activated sludge
6.	ARCO	Philadelphia, Pa.	B	activated sludge

The purpose of this pilot scale screening study is to determine if granular activated carbon possesses the capability to adsorb any of the priority pollutants and the treatment effectiveness encountered when powdered activated carbon is used to supplement a biological treatment system which is treating petroleum refinery wastewaters.

There are two general types of activated carbon treatment which are being investigated during this screening study. The granular carbon system consists of placing a bed of granular carbon in an enclosed container and percolating filtered biotreated water through the bed in the downflow mode. The second system is a powdered activated carbon system, where the powdered carbon is mixed with the mixed liquor of an activated sludge system.

A. Granular Activated Carbon System

During this screening, three virgin activated carbons from three carbon manufacturers and one activated carbon, which had been previously used at a refinery's activated carbon system and regenerated for recycle, are being investigated.

The refinery's bio-effluent is pumped through a multi-media filter column to remove suspended solids, insoluble oils, and pin point floc and scum which may be in the final effluent. The multi-media thick wall glass column is 5 ft. in length and 6 in. in diameter. On the bottom of the filter column is a stainless steel screen. Three inches of limestone rock are placed on the screen followed by 6 in. of washed sand and 18 in. of anthrafilt media for the top layer. Figure 7 is a diagram of the filter system used during the carbon screening study. When the pressure in the column exceeds 15 psig, the column is backwashed with either potable or carbon treated water, and an alternate multi-media filter is used to supply filtered bio-effluent to the carbon columns.

RSKERL has been supplied with virgin granular activated carbon from the following manufacturers who recommended the specific carbon to be used to treat petroleum refinery effluent:

1. Calgon Filtrasorb 300, 8 x 30 mesh
2. ICI Hydrodarco 3000, 8 x 30 mesh
3. Wesvaco WVG, 12 x 40 mesh

In addition to these three carbon sources, the Atlantic Richfield Co. (ARCO) supplied a source of Calgon's Filtrasorb 300 carbon which had been used and regenerated at ARCO's Watson Refinery's activated carbon treatment system. Figure 8 is a schematic of the granular carbon pilot scale system designed for this study.

Each column has a stainless steel sieve screen in the bottom of the column with 3 in. of limestone serving as a support bed for the specific carbon. Fifteen pounds of activated carbon was placed on top of the limestone rock for a carbon bed depth of 36 to 40 in. Multi-media filtered effluent is pressured into the top of each of the columns and the water percolates through the column into the discharge pipe which contains a valve limiting the flow to 0.25 g/m for each column. Figure 9 is a schematic of the granular carbon pilot system.

An alternate carbon system employing powdered activated carbon treatment is being evaluated at the four refineries where activated sludge treatment is employed. In this system, powdered activated carbon is added directly into the mixed liquor basin, and the carbon residual maintained at 4000 mg/l.

RSKERL designed and fabricated a 0.25 g/m complete mix activated sludge system from carbon steel. A schematic of the powdered carbon pilot scale system is shown in Figure 10. To acclimate the pilot system, mixed liquor from the refinery's aeration basin is pumped into the pilot plant's aeration basin, and the refinery's return sludge is added to the clarifier. Concentrations of suspended solids in the mixed liquor tank are maintained to approximate the full-scale plant's operation. During the initial period of acclimation in the pilot plant, the biological plant influent will be fed to the pilot scale aeration basin. Total organic carbon analyses are used to determine if the pilot scale effluent quality is essentially the same as the full-scale system.

On Day 5 of the study, five pounds (2,250 grams) of the selected powdered carbon, which was predetermined by an isotherm selection procedure, will be added to the inlet of the bio-plant in a slurry over a 10-hour time period.

Effluent from the final clarifier is collected in a sump; the water from the sump flows through glass wool to catch any powdered carbon which might be discharged. The glass wool and sump are emptied back into the aeration basin, thereby maintaining a near constant powdered carbon concentration in the pilot system.

CARBON SCREENING SAMPLING

Priority Pollutant Program

Screening samples are obtained from the intake, API separator, and NPDES sources on three consecutive days; the protocol, preservation, and procedures are the same as accomplished with the first six refineries. These same samples will be obtained on the sixth day, ninth day, twelfth day, and fifteenth day. A schedule of sampling periods for the priority pollutants is shown in Table 6.

Beginning with Day 6, the carbon screening pilot plant will be sampled and again on Days 9, 12, and 15. The sampling frequency and sampling location program is shown in Table 7.

The collected samples are air-freighted to Ada in ice chests. Upon receipt of the samples, phenolics and cyanides are analyzed to meet 24-hour preservation criteria. The three 24-hour composite non-volatile organics samples are composited into one sample and extracted in accordance with the March protocol. The extracts are forwarded to a contract laboratory for GC/MS analysis. Metals samples are digested and analyzed by the March protocol procedures and forwarded to EPA's Region V Laboratory where they will be analyzed by plasma emission spectrometer for comparative purposes. The three 24-hour volatile organics samples are composited and the composite forwarded to a contract laboratory for analysis. Split extracts for the non-volatiles are sealed in glass ampules and maintained a 4°C, and will be analyzed by an EPA laboratory to provide quality control information on the study.

During the carbon study, total organic carbon analysis is obtained every eight hours on the influent to the mixed-media filter and the effluents from the mixed-media filter activated carbon columns 1, 2, 3, 4, plus the pilot scale activated sludge influent and final effluent.

In addition to the priority pollutants, Effluent Guidelines Division contracted laboratory analyses for the same "classic parameters" that were analyzed in the Phase I screening study.

A final report will be prepared which will, in essence, report all analytical data obtained at each refinery, the refinery's data, analytical quality control, and description of the refinery, crude oil sources, etc.

REFERENCES

(1) Public Law 92-500, 92nd Congress, S. 2770, October 18, 1972, Page 1.

DISCUSSION

F. L. Robertaccio: The methodology used for the "carbon-biological" system being screened in this study is insufficient to be an adequate representation. I would like your comments on this remark and your opinion on how the aspect of your study might effect selection of models for establishment of effluent guidelines.

Leon H. Myers: First, I don't know how it will affect guidelines, that is out of my baliwick; I am in the research department. I mentioned, and I mentioned on purpose, that we only had three constraints. Time, money, and manpower. We are at each refinery 15 days, about four of those days are taken up in the initial screening. That leaves about 10 days that we are there running the carbon systems. I can't disagree with you, we can't get one good sludge age, much less two or three sludge ages to look at the powdered system at all. In my opinion, to use any of this data, you would have to use it very carefully. You have to remember that we are operating at a quarter GPM over a small time period. Our inclination is that we need at least a 10 GPM pilot scale study conducted parallel with the full-scale pilot scale study on powdered activated carbon and about 10 GPM granular carbon study conducted at the same plant, over about a year's period of time because of seasonal variations. We have discussed this with the effluent guidelines personnel and with research headquarters personnel. We haven't found anyone to disagree with us, we also haven't found any funding response Does that answer your comments?

BIOGRAPHY

Leon H. Myers holds a BS in Chemistry/Biology from Southwestern Oklahoma State University and a MS in Sanitary Science from Oklahoma University. He is currently Chief, Industrial Sources Section, of the Source Management Branch at the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma.

TABLE 1. SETTLEMENT AGREEMENT LIST OF 65 POLLUTANTS

Acenaphthene

Acrolein

Acrylonitrile

Aldrin/Dieldrin

Antimony and compounds

Arsenic and compounds

Asbestos

Benzene

Benzidine

Beryllium and compounds

Cadmium and compounds

Carbon tetrachloride

Chlordane (technical mixture and metabolites)

Chlorinated benzenes (other than dichlorobenzenes)

Chlorinated ethanes (including 1, 2-dichloroethane, 1,1,1-trichloroethane, hexachloroethane)

Chloroalkyl ethers (chloramethyl, chloroethyl, and mixed ethers)

Chlorinated naphthalene

Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)

Chloroform

2-chlorophenol

Chromium and compounds

Copper and compounds

Cyanides

DDT and metabolites

Dichlorobenzenes (1,2-,1,3-, and 1,4-dichlorobenzenes)

Dichlorobenzidine

Dichloroethylene (1,1-and 1,2-dichloroethylene)

2,4-dichlorophenol

Dichloropropane and dichloropropene

2,4-dimethylphenol

Dinitrotoluene

Diphenylhydrazine

Endosulfan and metabolites

Endrin and metabolites

Ethylbenzene

Fluoranthene

Haloethers (other than those listed elsewhere; includes chlorophenyphenyl ethers, bromophenylphenyl ether, bis (dischloroisopropyl)ether, ether, bis-(chloroethoxyl) methane and polychlorinated diphenyl ethers)

Halomethanes (other than those listed elsewhere; includes methylene chloride, methylchloride, methylbromide, bromoform, dichlorobromomethane, trichlorofluoromethamne, dichlorodifluoromethane)

Heptachlor and metabolites

Hexachlorobutadiene

Hexachlorocyclohexane (all isomers)

Hexachlorocyclopentadiene

Isophorone

Lead and compounds

Mercury and compounds

Naphthalene

Nickel and compounds

Nitrobenzene

Nitrophenols (Including 2,4-dinitrophenol, dinitrocresol)

Nitrosamines

Pentachlorophenol

Phenol

Phthalate esters

Polychlorinated biphenyls (PCBs)

Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes, and indenopyrenes)

Selenium and compounds

Silver and compounds

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

Tetrachloroethylene

Thallium and compounds

Toluene

Toxaphene

Trichloroethylene

Vinyl chloride

Zinc and compounds

TABLE 2. SPECIFIC COMPOUNDS

Compound

1. *acenaphthene
2. *acrolein
3. *acrylonitrile
4. *aldrin
5. *dieldrin
6. *benzene
7. *benzidine
8. *carbon tetrachloride (tetrachloromethane)
9 *_chlordane_ (technical mixture & metabolites)

Chlorinated benzenes (other than dichlorobenzenes)

10. chlorobenzene
11. 1,2,4-trichlorobenzene
12. hexachlorobenzene

Chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane and hexachloroethane)

13. *1,2-dichloroethane
14. *1,1,1-trichloroethane
15. *hexachloroethane
16. 1,1-dichloroethane
17. 1,1,2-trichloroethane
18. 1,1,2,2-tetrachloroethane
19. chloroethane

Chloroalkyl ethers (chloromethyl, chloroethyl and mixed ethers)

20. *bis(chloromethyl) ether
21. *bis(2-chloroethyl) ether
22. 2-chloroethyl vinyl ether

Chlorinated naphthalene

23. 2-chloronaphthalene

1-bromodecane Std.
1-bromododecane Std.

Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)

24. 2,4,6-trichlorophenol
25. _p_-chloro-_m_-cresol

26. *chloroform (trichloromethane)

27. *2-chlorophenol

DDT and metabolites

28. *4,4'-DDT
29. 4,4'-DDE
30. 4,4'-DDD (p,p'-TDE)

Dichlorobenzenes (1,2-;1,3-; and 1,4-dichlorobenzenes)

31. *1,2-dichlorobenzene
32. *1,3-dichlorobenzene
33. *1,4-dichlorobenzene

Dichlorobenzidine

34. 3,3'-dichlorobenzidine

Dichloroethylenes (1,1-dichloroethylene and 1,2-dichloroethylene)

35. *1,1-dichloroethylene
36. *1,2-trans-dichloroethylene

37. *2,4-dichlorophenol

Dichloropropane and dichloropropene

38. 1,2-dichloropropane
39. 1,3-dichloropropylene (1,3-dichloropropene)

40. *2,4-dimethylphenol

Dinitrotoluene

41. 2,4-dinitrotoluene
42. 2,6-dinitrotoluene

43. *1,2-diphenylhydrazine

Endosulfan and metabolites

44. *α-endosulfan
45. *β-endosulfan
46. endosulfan sulfate

Endrin and metabolites

47. *endrin
48. endrin aldehyde
49. endrin ketone

50. *ethylbenzene
51. *fluoranthene

Haloethers (other than those listed elsewhere)

52. *4-chlorophenyl phenyl ether (p-chlorodiphenyl ether)
53. *4-bromophenyl phenyl ether
54. *bis (2-chloroisopropyl) ether
55. *bis (2-chloroethoxy) methane

Halomethanes (other than those listed elsewhere)

56. *methylene chloride (dichloromethane)
57. *methyl chloride (chloromethane)
58. *methyl bromide (bromomethane)
59. *bromoform (tribromomethane)
60. *dichlorobromomethane
61. *trichlorofluoromethane
62. *dichlorodifluoromethane
63. chlorodibromomethane

Heptachlor and metabolites

64. *heptachlor
65. heptachlor epoxide

66. *hexachlorobutadiene

Hexachlorocyclohexane (all isomers)

67. *α-BHC
68. *β-BHC
69. *γ-BHC (lindane)
70. *δ-BHC

71. *hexachlorocyclopentadiene
72. *isophorone
73. *naphthalene
74. *nitrobenzene

Nitrophenols (including 2,4-dinitrophenol and dinitrocresol)

75. 2-nitrophenol
76. 4-nitrophenol
77. *2,4-dinitrophenol
78. 4,6-dinitro-*o*-cresol

Nitrosamines

79. N-nitrosodimethylamine
80. N-nitrosodi-n-propylamine
81. N-nitrosodiphenylamine

82. *pentachlorophenol
83. *phenol

Phthalate esters

84. bis (2-ethylhexyl) phthalate
85. butyl benzyl phthalate
86. di-n-butyl phthalate
87. diethyl phthalate
88. dimethyl phthalate

Polychlorinated biphenyls (PCB's)

89. *PCB-1242 (Arochlor 1242)*
90. *PCB-1254 (Arochlor 1254)*

Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes, and indenopyrenes)

91. 1,2-benzanthracene
92. benzo[a]pyrene (3,4-benzopyrene)
93. 3,4-benzofluoranthene
94. 11,12-benzofluoranthene
95. *chrysene
96. acenaphthylene
97. anthracene
98. 1,12-benzoperylene
99. fluorene
100. phenanthrene
101. 1,2:5,6-dibenzanthracene
102. indeno (1,2,3-C,D)pyrene
103. pyrene

104. *2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)
105. *tetrachloroethylene
106. *toluene

107. _*toxaphene_

108. *trichloroethylene
109. *vinyl chloride (chloroethylene)
1-bromodecane (possible internal standard)
1-bromododecane (possible internal standard)

TOTAL METALS

1. Arsenic
2. Beryllium
3. Cadmium
4. Chromium
5. Lead
6. Mercury
7. Nickel
8. Thallium
9. Antimony
10. Copper
11. Selenium
12. Silver
13. Zinc
14. Asbestos
15. Cyanides

Table 3

REFINERIES SELECTED FOR THE PRIORITY POLLUTANT STUDY

Refinery	Location	Refinery Class	Treatment System
Gulf	Philadelphia, Pa.	C	Trickling Filter Activated Sludge
Exxon	Baytown, Tex.	E	Aerated Lagoon
Hunt	Tuscaloosa	A	Activated Sludge
Clark	Hartford, Ill.	B	Activated Sludge Filtration
Texaco	Lockport, Ill.	B	Activated Sludge
Mobil	Augusta, Kan.	B	Oxidation
Phillips	Sweeney, Tex.	C	Aerated Lagoon
Shell	Anacortes, Wash.	B	Activated Sludge
Exxon	Benecia, Calif.	B	Activated Sludge
Exxon	Billings, Mont.	C	Aerated Lagoon
Coastal States	Corpus Christi, Tex.	C	Activated Sludge
ARCO	Philadelphia, Pa.	B	Activated Sludge

Table 4

PRIORITY POLLUTANTS SAMPLING INFORMATION

Parameter	24-hour Composite	Grab Sample	Sample Container	Preservative
Non Volatile	X		1 Gallon Glass	Ice
Metals	X		1 Gallon Plastic	HNO_3
Mercury		X	1 Quart Plastic	HNO_3
Cyanide		X	1 Quart Plastic	NaOH
Phenolics		X	1 Quart Glass	H_3PO_4
Asbestos		X	1 Quart Plastic	Ice
Volatile		X	40 ml Vial	Ice

Table 5

CLASSICAL PARAMETERS SAMPLING INFORMATION

Parameter	24-hour Composite	Grab Sample	Sample Container	Preservative
BOD_5	X		Plastic	Cool 4°C
TSS	X		Plastic	Cool 4°C
COD	X		Plastic	H_2SO_4 to pH<2
TOC	X		Plastic	H_2SO_4 to pH<2 Plus Cool, 4°C
NH_3-N	X		Plastic	H_2SO_4 to pH<2 Plus Cool, 4°C
Cr^6	X		Plastic	HNO_3 to pH<2
Sulfide	X		Plastic	2 ml Zinc Acetate
Oil & Grease		X	Glass	H_2SO_4 to pH<2 Plus Cool, 4°C

Table 6

SCHEDULE OF SAMPLING PERIODS

Day	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	W	Th	F	S	Su	M	T	W	Th	F	S	Su	M	T	W	Th	F
	S	S	S	S		S			S			S			S		
	C	C	C	C		C			C			C			C		
	R	R	R	R		R			R			R			R		
	E	E	E	E		E			E			E			E		
	E	E	E	E		E			E			E			E		
	N	N	N	N		N			N			N			N		

Sample locations are depicted in Figure 11.

Table 7

SAMPLING FREQUENCY AND LOCATION PROGRAM

	Day						
Sample Site	1	2	3	6	9	12	15
Intake	X	X	X				
Separator	X	X	X				
Bio-Effluent	X	X	X	X	X	X	X
Mixed-Media Filter Eff.				X	X	X	X
Activated Carbon Eff.				X	X	X	X
Regenerated Carbon Eff.				X	X	X	X
Activated Sludge/Activated Carbon Influent				X	X	X	X
Activated Sludge/Activated Carbon Eff.							

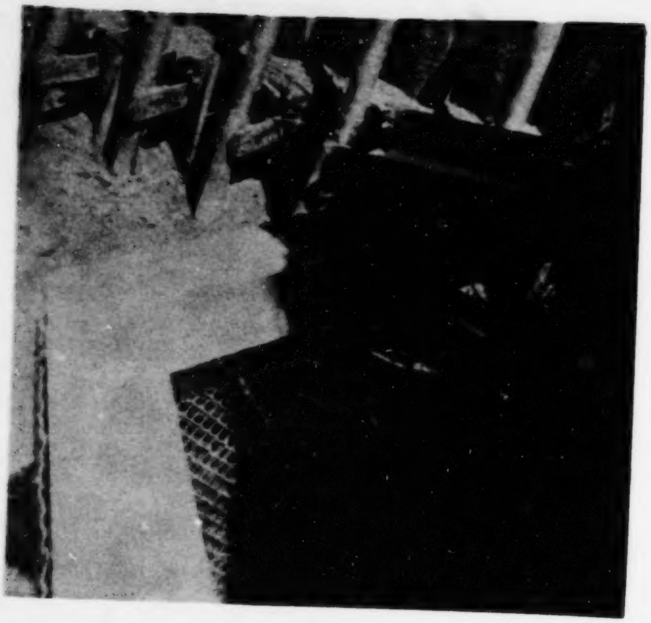

Figure 1. INTAKE SCREEN HOUSE

Figure 2. INTAKE WATER SAMPLE POINT

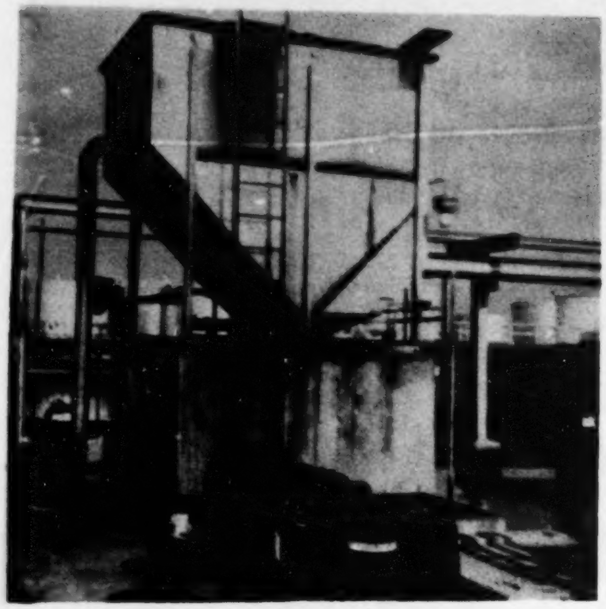

Figure 3. Corrugated Plate Interceptor-Hunt/Tuscaloosa

Figure 4. Bypass Line From Corrugated Plate Interceptor Hunt/Tuscaloosa

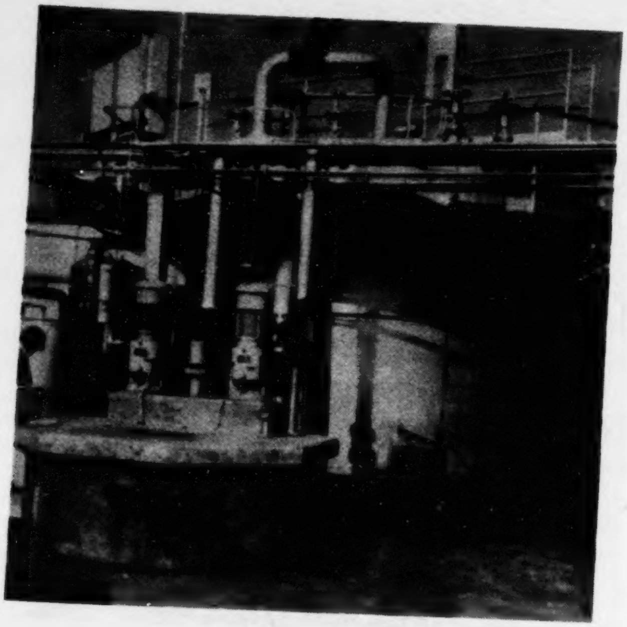

Figure 5. DAF Unit-Hunt/Tuscaloosa

Figure 6. Final Effluent-Hunt/Tuscaloosa

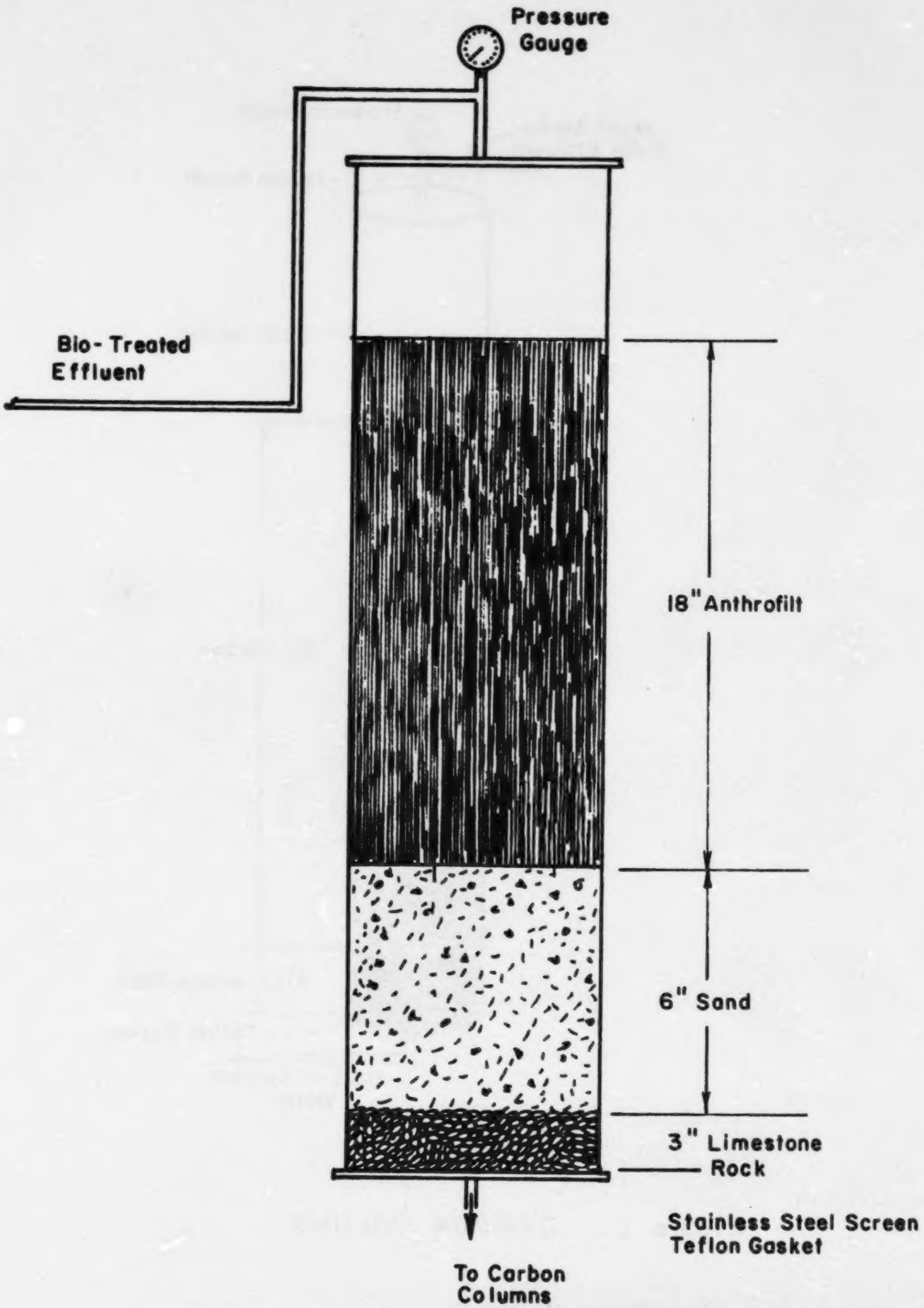

Figure 7. MIXED-MEDIA FILTER DIAGRAM

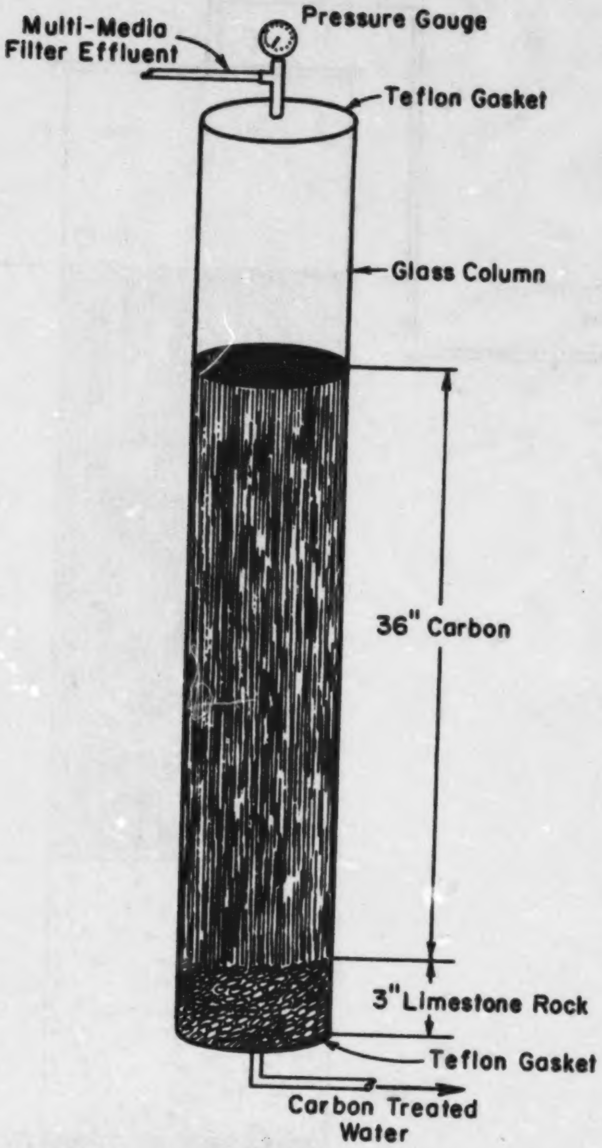

Figure 8. CARBON COLUMN

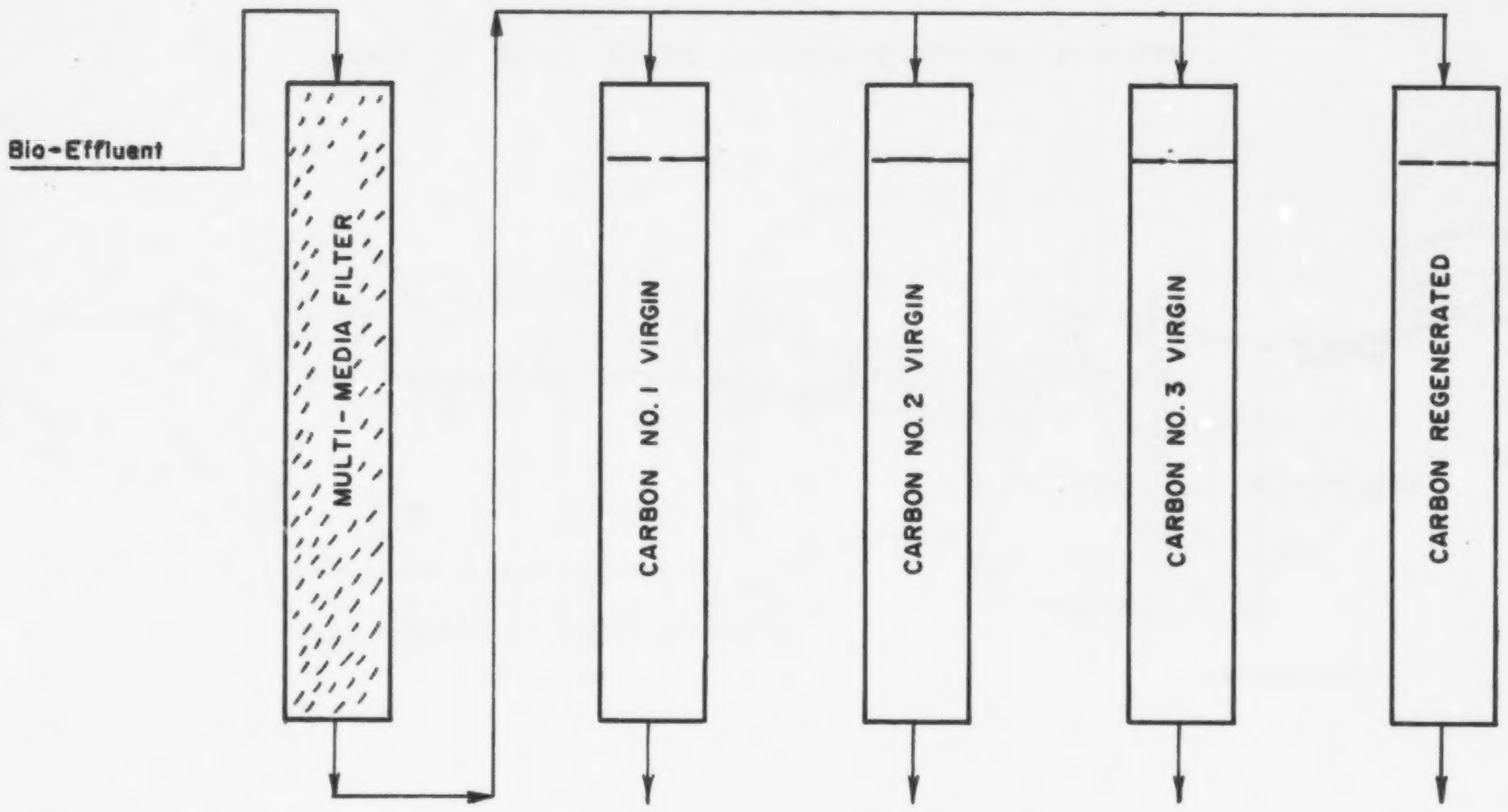

Figure 9. PILOT CARBON SYSTEM

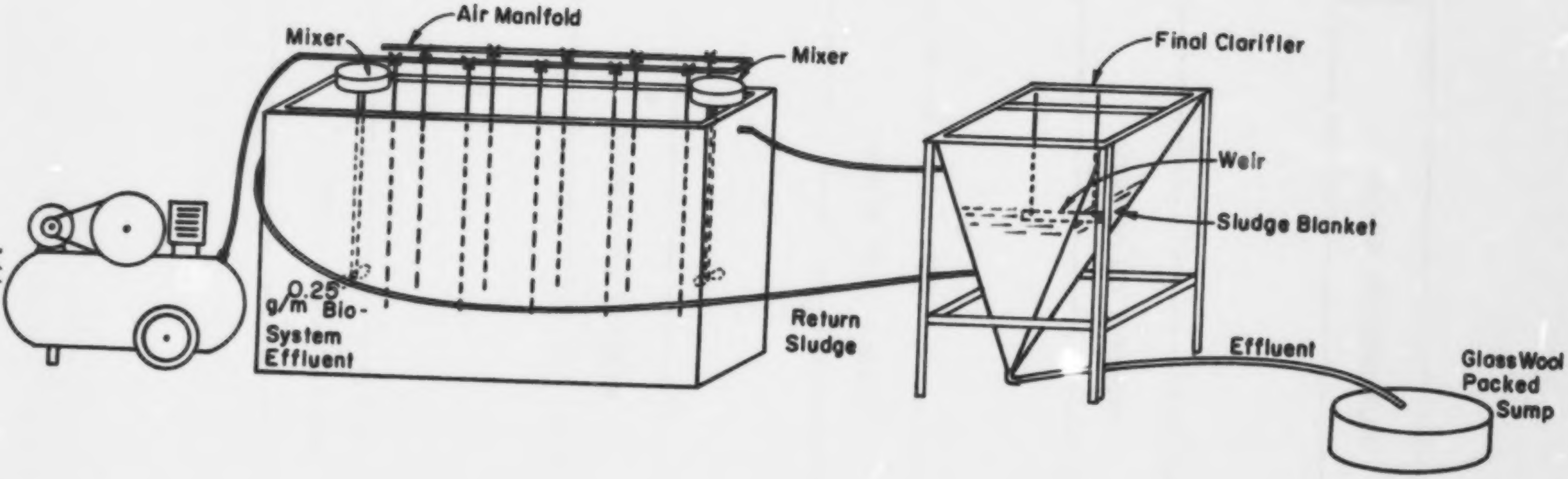

Figure 10. PILOT SCALE ACTIVATED SLUDGE SYSTEM

"CONSIDERATIONS FOR DEFINING SUBSTANCES HAZARDOUS TO THE ENVIRONMENT"

A. Karim Ahmed
Staff Scientist, Natural Resources Defense Council

I am pleased to be here today to address this conference about one of the most important programs embarked upon by the federal government to regulate the proliferation of toxic substances in our environment. This morning, Mr. Ridgeway Hall of the Environmental Protection Agency (EPA) gave us an excellent presentation of the events that led to the settlement agreement - known to some of us as The Consent Decree - between the Natural Resources Defense Council (NRDC) and other environmental groups and the EPA. This out of court settlement, which was approved by the U.S. District Court for the District of Columbia on June 9, 1976,[1] is a wide-ranging regulatory strategy, with a clearly defined timetable, for controlling the discharge of toxic substances into our nation's waterways, as required under the Federal Water Pollution Control Act (FWPCA).[2] Since we have heard a good deal about EPA's present and proposed implementation of the Consent Decree from Mr. Hall and other speakers, I will attempt to give you a somewhat different overview of the same subject matter - namely the problem we face when we wish to define substances that are hazardous to the environment. I will do so in the context of reviewing with you some of the major federal statutes that deal with the hazardous or toxic substances issue.

I would like to conceptually divide major federal statutes that have dealt with the problems of toxic substances in the past and do so currently into two main divisions: (1) statutes that primarily address toxic substances in terms of their effects on human health, and (2) statutes that were intended to regulate the impacts of toxic substances on the environment. Now I have purposely divided this into black-and-white terms and I will try to explain to you why. First, let's look at the statutes that deal with problems of human health. These generally come under the purview of the Food and Drug Administration, under the Food, Drug and Cosmetic Act;[3] the Department of Labor, under the Occupational Safety and Health Act;[4] and the Consumer Product Safety Commission, under the Consumer Product Safety Act,[5] and the Federal Hazardous Substances Act.[6] These statutes, which I will explain as we go along, primarily deal with effects on human health, and are regulated by the three federal agencies I have just mentioned.

On the other hand, the EPA, which was created in the early 70's through the reorganization of the federal bureaucracy, was given jurisdiction to regulate impacts on the environment. However, as we have now discovered, the environment also includes man. The EPA has a particularly difficult task in trying to define toxic substances which have, first of all, an impact on the environment, and secondly, an impact on human health, or both. The various statutes that EPA has authority under are the Federal Water Pollution Control Act,[7] the Clean Air Act,[8] the Toxic Substances Control Act,[9] the Safe Drinking Water Act,[10] the Resource Conservation and Recovery Act,[11] and the Ocean Dumping Act.[12] EPA also regulates pesticides under the Federal Insecticide, Fungicide and Rodenticide Act.[13]

The problem that we're faced with here is essentially one of overlapping jurisdiction. Let me give you examples of some of the problems we have had of late. When the issue of fluorocarbon's impact on stratospheric ozone was first brought to the attention of the federal agencies, we had complete chaos. In fact, the first thing that the agencies did was to run to the Department of Justice to ask for a memorandum that would sort out the issue of legal jurisdiction. The Natural Resources Defense Council had petitioned the Consumer Product Safety Commission (CPSC) who, in spite of having jurisdiction over only about five to ten percent of the total aerosol products on the market, had strong regulatory authority under the Consumer Product Safety Act.[14] When we confronted them with our petition, the Commission argued at first that the problem was one of environmental concern and only indirectly would affect human health - i.e. the increase of ultra-violet radiation, caused by environmental loss of ozone would indirectly lead to an increase in skin cancer incidence. So, the CPSC felt that it really didn't fit under their jurisdiction. Similarly, the FDA said that they had statutory authority with foods, drugs, and cosmetics as they affect human health directly, but had not been given authority to deal with environmental issues. Lastly, the EPA put a final ironic twist to this regulatory comedy by claiming that under the Clean Air Act it had jurisdiction on the lower atmosphere only. They were not sure about the stratosphere; perhaps some other agency dealt with the upper atmosphere. So this classic "passing-the-buck" game began back in 1974. At that time, this issue was too new and unfamiliar, and somewhat controversial, for any agency to want to handle. We had a really troublesome situation where none of the agencies knew where their jurisdiction lay and how they should go about regulating products under statutes that defined their authority narrowly, or at best, ambiguously.

Another example, which is just beginning to emerge, is the problem of genetic engineering. In genetic engineering, we have a naturally occurring substance called DNA which, as you know, is the subject of biological manipulation. One would surely think that the Department of Health, Education and Welfare, under the U.S. Public Health Service Act,[15] would have clear jurisdiction on this issue since, under credible experimental conditions, new life forms may be produced, such as a bacterial system that could be potentially infectious. But the EPA now claims that, under the Toxic Substances Control Act (TSCA), DNA may be defined as a chemical substance. Consequently, under certain provisions of

TSCA, it may have jurisdiction. Here, they're claiming jurisdiction, rather than avoiding it. In a sense, we have another potential conflict here - one of asserting jurisdiction.

With respect to the fluorocarbon-ozone issue that I mentioned earlier, what subsequently happened was a formation of an inter-agency committee under the auspices of the Council on Envi-ronmental Qulaity (CEQ) leading to a thorough study by the National Academy of Sciences.[16,17] A few months ago, as you know, all three agencies (the CPSC, and FDA and the EPA) jointly proposed regulations governing the ban of fluorocarbons as propellants in aerosol products.[18] For the first time, a kind of cooperative regulatory venture is being experimented with by the federal agencies on a hazardous substance that does not fit under neatly defined jurisdictions.

There are, on the other hand, some hazardous chemical substances that appear to be clearly defined under different statutes. Let me give you an example - asbestos is one of the best. If one has a problem of asbestos in water, one would go to the EPA, since under the Federal Water Pollution Control Act or the Safe Drinking Water Act they have jurisdiction.[19] If it's an air related problem, then one would also go to the EPA, for under Section 112 of the Clean Air Act, they have promulgated regulations with respect to asbestos emissions.[20] If it's a problem in consumer products, for example, in spackling compounds, artificial fireplace logs, or asbestos-containing ceiling tile, one would go to the Consumer Product Safety Commission which has jurisdiction either under the Consumer Product Safety Act or the Federal Hazardous Substance Act.[21] If it's a matter of asbestos in talcum powder or toiletries, one would go to the FDA who have clear authority under the Food, Drug and Cosmetic Act.[22] It it's a labeling question - a label to warn consumers - one would go to one of the line agencies or directly to the Federal Trade Commission (FTC) which could issue regulations under the Federal Fair Labeling and Packaging Act.[23] If it's a workplace hazard, one would go to the Department of Labor's Occupational Safety and Health Administration for setting up occupational standards.[24] And finally, if it's a universal problem, one would go back to the EPA. Why? Because they now have the Toxic Substances Control Act,[25] enacted into law last year, which is supposed to take care of everything generically and completely. So, the EPA has the biggest task again.

Let's get down to specifics in defining substances that are hazardous. One way of defining substances that are hazardous to the environment is to look at it in a narrow "legal" sense. It is reasonable to expect that the statutes were written at different times for different reasons, since the congressional intent for enacting such laws tend to be rather different. But when one examines the various statutes on the books, one finds that some of the laws do not have an explicit definition of what is meant by the term "toxic." They might, for example, address the issue of toxicity by alluding to questions of safety and unsafety in very general terms. This is particularly true with the Federal Food, Drug and Cosmetic Act (FDCA). The FDCA has lengthy sections on procedural matters, about burden of proof, etc., but the actual definition of toxic substances is never made clear. This also appears to be the case under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), which has no definition of what is a hazardous or harmful pesticide. However, a clearer statement about hazardous substances can be found in the Federal Hazardous Substances Act (FHSA). This particular Act is interesting because it defines "hazardous" in very narrow terms and yet has broad application. Under Section 2(f) of the FHSA, "hazardous substance" means:

> "Any substance or mixture of substances which is (1) toxic, (2) corrosive, (3) an irritant, (4) a strong sensitizer, (5) flammable or combustible, and (6) generates pressure through decomposition, heat or other means, if such substances or mixtures may cause substantial injury or substantial illness...."

Notice here that the definition deals with either health or safety of human beings. It does not deal with environmental issues. (This is an important section of the Act because later I will go back to it when I talk about a proposed EPA regulation.) Under Section 2(g) of the same Act, we have a definition of what is "toxic:"

> "Any substance (other than a radioactive substance) which has the capacity to produce injury or illness to man through ingestion, inhalation or absorption through any body surface."

Here, again, toxic is defined with respect to human beings. In Section 2(h), we have a definition of "highly toxic," which is defined in terms of three explicit guidelines that are employed in animal tests: (1) for ingested substances, an LD_{50} value which is equal to or less than 50 milligrams per kilogram; (2) for inhaled substances, an LC_{50} figure which is equal to or less than 200 parts per million, or 2 milligrams per liter; and (3) dermal absorption, an LD_{50} figure equal to or less than 200 milligrams per kilogram. We have here a definition of "toxic" or "highly toxic" in a very conventional sense of the term - meaning acute animal or human toxicity. There is no reference to chronic toxicity, nor does it refer to environmental harm of any kind. Obviously, the intent of this Act was to regulate products or substances that would acutely injure human beings.

We should now examine statutes that simultaneously deal with human and environmental effects. The best place to start, I think, is the Toxic Substances Control Act which, even though it is the most recently passed law, is causing a great deal of confusion in the minds of a lot of people who have to deal with this statute. Let us examine whether we have any definition of a hazardous or toxic substance in this Act. It first occurs under Section 4, which is the section that deals with testing of chemical substances and mixtures, and here it is basically defined in terms of substance or mixture which "may present an unreasonable risk of injury to health or the environment." That is, the definition is very broad. In subsection (2)(A) of Section 4, mention is made of the kinds of standards or testing that would be required to assess what is "unreasonable" - that is, what are the unreasonable risks to health and the environment - and mentioned are tests for carcinogenesis, mutagenesis, teratogenesis, behavioral disorders, cumulative or synergistic disorders, etc., in addition to requiring testing for acute toxicity, subacute toxicity, and other chronic toxicity. The same definition occurs again under Section 6 of the Act, which is the section that deals with the actual regulation of hazardous substances, that provides the agency with the authority to remove a toxic substance from the marketplace:

> "If the Administrator finds that there is a reasonable basis to conclude that the manufacture, processing, distribution in commerce, use, or disposal of a chemical substance or mixture, or that any combination of such activities, presents or will present an unreasonable risk of injury to health or the environment, the Administrator shall by rule apply one or more of the following requirements to such a substance or mixture...."

Finally, in Section 7 of the Toxic Substances Control Act, we have the Imminent Hazards section which, I think, is an important provision to recognize. Here, the Administrator is given certain additional powers to commence action when substances or mixtures possess an "imminent or unreasonable risk of serious or widespread injury to health or the environment." And, once again, the theme is both health and the environment.

We shall now examine the Federal Water Pollution Control Act and see how clearly the term "hazardous substance" is defined. We find that we really do not have an unequivocal answer. In a sense, it is a bit of a mess because when one examines the FWPCA even an experienced environmental attorney has a difficult time in figuring out what the correct definitions are. Apparently the only place in the FWPCA where the term "toxic pollutant" is defined is under Section 502, paragraph 13:

> "The term 'toxic pollutant' means those pollutants or combination of pollutants including

> disease causing agents which...on the basis of information available to the Administrator, cause death, disease, behavioral abnormalities, cancer, genetic mutations, physiological malfunctions (including malfunctions in reproduction) or physical deformities, in such organisms or their offspring."

It would appear to be all inclusive. One would not use such a broad definition to select a list of highly toxic pollutants. However, this is the manner by which "toxic pollutant" has been defined under Section 307(a), which deals with the development of effluent standards of toxic pollutants in the FWPCA. The prohibition of toxic pollutants in toxic amounts is clearly stated in Section 101(a)(3) of the Act which, when combined with Section 502(13), gives us the "correct" intent of Section 307(a). This is apparently the way the concept of "toxic pollutant" is defined under the Act.

In Section 311 of the FWPCA, on the other hand, we see a completely different approach since it deals with the liability of an accidental spill. But it has a broad definition of "discharge" in this section, for it "includes, but is not limited to spilling, leaking, pumping, pouring, emitting, emptying, or dumping." One would think that Section 311 would be even more all-inclusive in terms of point discharges than accidental spills; moreover, it goes on to define "hazardous substances" as those that may "present an imminent and substantial danger to the public health or welfare including, but not limited to, fish, shell-fish, wildlife, shoreline and beaches." Interestingly enough, there is also a provision in the FWPCA giving the Administrator certain emergency powers under Section 504, where a similar language is repeated, i.e. "presenting an iminent and substantial endangerment to the health of persons and to the welfare of persons...." What we have here is a provision that, on the one hand, appears to be quite restrictive in defining emergency powers of the Administrator and, at the same time, defines hazardous substances quite broadly. We must therefore ask: which of the two statutory "sets" is greater? Is Section 307(a) a "subset" of Section 311; are they two separate, disjunctive "sets;" or do they overlap? We don't really have clear answers to this, in part because we don't have a Section 311 regulation promulgated as yet. This only compounds the present regulatory confusion.

Let us now examine the problem of defining "hazardous substance" from a more technical or scientific point of view. In the past, promulgated regulations, reflecting the intent of federal statutes, emphasized acute toxicity - for example, the Federal Hazardous Substances Act which, as I mentioned earlier, only dealt with short-term acute toxicity and defined toxicity in terms of LD_{50}'s and LC_{50}'s, etc. More recently, there has been a growing concern about long-term chronic effects and consequently about carcinogenic and mutagenic effects. These toxic substances exert their effects over a long time period when ingested in small amounts by man or animal and may cause cancer with latency periods of 20 to 40 years. As Mr. Hall mentioned this morning, that was one of the chief criteria used in selecting the priority chemical substances under the settlement agreement. We are also concerned with certain key environmental factors when defining hazardous substances. These are generally questions of: (1) chemical persistence - biological and chemical degradibility, (2) movement in the environment, i.e., how does it get transported - by air, by water, or by soil, (3) bioconcentration in the environment, including biomagnification in the food chain, and (4) synergistic and cumulative effects of the chemical substance. These are all now becoming part and parcel of defining hazardous substances from a scientific point of view. In selecting substances to be regulated under the Consent Decree, all the above factors were given appropriate weight, and we hope led to a better selection process than had been used by the agency in the past.

Lastly, I will briefly mention our views on the Consent Decree. As you may recall, under Section 307(a) of the FWPCA, the EPA had ninety days to publish a list of toxic substances for which effluent standards were to be established. We interpreted this section of the Act to apply to those highly toxic or persistent substances for which there would be neither a technology-based nor an economically-based effluent standard. After initial litigation by NRDC, EPA in July 1973 proposed a list of nine substances to be regulated under Section 307(a) of the FWPCA. Most of the substances were pesticides, a few metal ions, and PCB. At administrative hearings held by the EPA, the agency was literally swamped with technical information from the affected industries that claimed that the agency did not have an adequate scientific basis for setting proposed new effluent standards. Consequently, the EPA abandoned their proposal and did not promulgate effluent standards under Section 307(a). NRDC filed additional suits against EPA, claiming that there were a large number of chemical substances (certainly greater than nine) that could be termed toxic or hazardous and ought to be regulated under Section 307(a).

To make a long story short, we finally ended in an out-of-court settlement which is now known as the Consent Decree. In arriving at the Consent Decree, it is very interesting to note some of the issues that were agreed to by both sides. There was a recognition that there were different provisions in the FWPCA that could regulate toxic substances, and that Section 307(a) was not necessarily the only handle that should be used. These additional provisions include Sections 301, 304 and 306. The basis for developing a priority list under this concept was that the agency was given more flexibility in dealing with toxic substances, some of which have only recently been shown to have potential long term problems of carcinogenicity and mutagenicity. Thus, instead of using Section 307(a) as the only basis for regulating toxic substances, with its limited timetable schedules and larger burden of proof on the agency, EPA would use a combination of different provisions under the FWPCA, using a technology-based and New Source Performance Standard approach as provided for in Section 306. What we have now is a list of some 129 chemical compounds that have been identified as priority substances. Effluent standards for six substances have already been promulgated under 307(a) provisions (as required under the Consent Decree) and the standards for the remaining substances will be issued under BAT (best available technology) provisions of the Act.

The big puzzle that now remains is the development of regulations under Section 311 of the FWPCA. The agency has proposed a list of substances to be regulated under Section 311, which, I think, is totally inadequate since most of the information on hazardous substances in the proposed regulations is based upon aquatic toxicity, and the agency has chosen to define Section 311 in those terms. And to make matters even more puzzling, EPA used the same criteria of defining toxicity as the Hazardous Substances Control Act which, as I mentioned earlier, only defined acute toxicity. The agency has essentially used the same LD_{50}, LC_{50} figures in arriving at their conception of what is acutely toxic to human beings. They have explicitly ignored questions of chronic effects as is clear from the preamble to the proposed regulations.[26] In fact, EPA has made a point of not being concerned with issues of chronic effects, for reasons which are totally unclear. Consequently, these proposed regulations are still pending and we do not know when they will be promulgated.

It is clear that whatever regulations will now be adopted under the FWPCA, we will have to be concerned both with the implementation of the Consent Decree and with the implementation of the Toxic Substances Control Act. For example, a major issue right now is the inventory reporting provision under TSCA. This provision requires EPA to obtain from the affected industries a complete knowledge of what chemical substances are being used, in what amounts, and for what purpose. Under the Consent Decree, EPA has been gathering similar information on substances on the priority list. These same questions have not been addressed by the agency under the Toxic Substances Control Act, where they are given authority to seek such information. EPA has been subjected to a lot of criticism by NRDC and others about the way they've gone about collecting this critical bit of information. In the final analysis, if we are to have meaningful control of the discharge of toxic substances into our environment, we will have to see a dovetailing of the effort between the Water Program staff of the EPA, who are implementing the Consent Decree program, and the staff of the Office of Toxic Substances, who are trying to implement the Toxic Substances Control Act. Only then can we have confidence in the ultimate success of EPA's program to control the ever growing impact of hazardous substances on the environment. Thank you very much.

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BIOGRAPHY

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SESSION V

PROBLEMS

Chairman

George J. Putnicki

Visiting Professor, Environmental Sciences
University of Texas at Dallas, Texas

Speakers

Dwight G. Ballinger
"EPA's Analytical Development Program for Problem Pollutants"

Fred T. Weiss
"Fates, Effects and Transport Mechanism of Pollutants in the Aquatic Environment"

Donald I. Mount
"Measuring Aquatic Impact of Toxic Contaminants"

Davis L. Ford
"An Overview of Advanced Treatment Systems"

BIOGRAPHY George J. Putnicki

George J. Putnicki is currently a Visiting Professor in the graduate programs in Environmental Sciences at the University of Texas at Dallas. He holds a B.S. in Civil Engineering from Marquette University and a M.S. from Oregon State University. Prior, Mr. Putnicki has had extensive experience in the EPA Region Six and was Deputy Regional Administrator and Director of the Hazard Materials Control and Surveillance Control Divisions.

Mr. Putnicki has received many awards and commendations from the EPA and is a registered P.E. in Oklahoma, Texas and Louisiana.

EPA'S ANALYTICAL DEVELOPMENT PROGRAM FOR PRIORITY POLLUTANTS

Dwight G. Ballinger, Director
Environmental Monitoring and Support Laboratory - Cincinnati

INTRODUCTION

Previous speakers in this Open Forum have discussed the details of the 1976 Consent Decree for priority pollutants and the development of a list of elements and compounds for which standards are to be set. I will focus my remarks on the analytical methods requirements involved in the implementation of the Decree and describe briefly what EPA is doing to meet these requirements.

Although the standards will be established by 1983, this will be only the first step in reducing the volume of these hazardous materials discharged to surface waters of the United States. The standards will be incorporated in permits administered by the states and EPA and the permit conditions will require the monitoring of waste discharges and the reporting of the volume and concentration of these pollutants in each discharge. Section 304(g) of the Federal Water Pollution Control Act requires the Administrator of EPA to promulgate test procedures for use in determining compliance with permit conditions. Under this section, an analytical method must be selected for each parameter listed in the permits and these procedures or an acceptable alternative, are to be used in all waste monitoring. Test procedures were first published in 1973 and were revised and expanded in the Federal Register of December 1, 1976. In practice, the list of analytical methods are first published as proposed, public comments are received and considered, and then the test procedures are published as final regulations. The methods in the original listing and later revisions were chosen in close cooperation with the state agencies, other federal agencies, and method standardization groups such as the committee for Standard Methods for the Examination of Water and Wastewater and ASTM Committee D-19. The petroleum industry is ably represented on Committee D-19 and the Committee has provided significant input to the selection of analytical methods.

Basically, the analytical methods requirements for the priority pollutants are the same as those for other pollutants....a proven,

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Presented at the Second Open Forum on Management of Petroleum Refinery Wastewater, Tulsa, Oklahoma, June 7, 1977 defensible test procedure for each of the elements and compounds for which standards are set and monitoring is required.

PROBLEM DEFINITION

Such a simple statement, however, is deceptive. A better perspective on the problem discloses a number of critical factors. The original list of 65 toxic substances contained a number of groups of organic compounds such as chlorinated benzenes, chlorinated phenols, haloethers, and polynuclear aromatic hydrocarbons. When each of the individual compounds in these groups are defined the list of specific compounds comes to about 120. If standards are set for each compound, a test procedure must be available for that compound. To meet the requirements for monitoring, test procedures for these compounds must be available by 1983. The majority of these procedures will require analysis for complex organic structures.

These constituents originate in a wide variety of industrial wastes including plastics manufacturing, the production of synthetic organic chemicals, and, of course, petroleum refining. The priority pollutants often occur as by-products rather than the principal product and are therefore in relatively small amounts. While most of them have been identified in waste streams, they have not often been measured in environmental samples with adequate precision and accuracy. Preliminary literature searchs have failed to produce the methodology required and a significant amount of new development will be necessary.

Among the list of compounds for which test procedures will be required are a number of interest to the petroleum industry. In the group of polynuclear aromatics are 16 individual compounds; there are 11 phenols and three nitrobenzenes on the list.

The anticipated maximum permissible concentrations in the permits have yet to be established since they will be dependent on the best available treatment, the relative toxicity, and other factors. These concentrations, however, will be minimal and the analytical "target" for methods development is 10 μg/l. Based upon previous work, even lower working ranges may be necessary to detect and measure the specific pollutants.

An appropriate test procedure must measure these concentrations of the pollutant with positive qualitative identification, in wastewaters containing many interferents of similar chemical structure and present in amounts 100 to 1000 times the measured constituent.

In addition, the test procedure should not be tailored to a particular wastewater, but should be applicable in all wastes where the pollutants can occur. This variety of substrates will require extensive separations and cleanup to achieve specificity in the test method.

Since the test procedure will be used by both the discharger and the regulatory agencies, it must be within the technical and economic capabilities of these laboratories. The method must be as simple as possible to minimize the workload, the instrumentation used must be readily available on the open market at reasonable cost, and there must be a sufficient number of analysts having the necessary skills and training to perform these analyses. These constraints are common to all test procedures promulgated for environmental monitoring and must be considered in the development and final selection of an analytical method to be used nationwide. While a test procedure developed in an academic laboratory may produce satisfactory results in the hands of the research scientist who developed it, it may not meet the needs for routine monitoring.

The problem for EPA and the task assigned to the Environmental Monitoring and Support Laboratory in Cincinnati is to have all these analytical methods available by June 30, 1983. By that time, under ideal conditions, the methods will have been thoroughly tested on a large number of actual wastes samples, subjected to round-robin testing by a group of environmental laboratories, have been widely disseminated for familiarization, and perhaps adopted by industry groups and the method standardization organizations as standard procedures.

We fully recognize the magnitude of the task and EPA is committed to applying its resources to see that methods are available to carry out the monitoring requirements inherent in the Consent Decree.

CURRENT STATUS OF METHODOLOGY

A number of elements and compounds identified as priority pollutants are now incorporated in discharge permits. Test procedures for these have been published in accordance with Section 304(g) of PL 92-500. The most recent amendments, published in December 1976, include approved methods for 16 of the 65 pollutants in the Consent Decree. Thus test procedures for all of the heavy metals and a few of the organics are already available and published. Methods development research at the Cincinnati laboratory has produced procedures for many of the common pesticides, chlorinated compounds, and volatile halogenated compounds. These methods are widely used and are being standardized and adopted by EPA, ASTM, and Standard Methods for the Examination of Water and Wastewater. They will be incorporated in the monitoring program as permit conditions require. At the time of the signing of the Consent Decree, methods had been developed for 34 of the 65 elements and compounds listed, although not all of the methods had been thoroughly tested in a variety of wastes and few of them had been subjected to interlaboratory study considered necessary for full documentation of the procedures.

METHODS DEVELOPMENT CONTRACTS

The methods research described has been conducted with limited resources. It is apparent that a crash program will be necessary to meet the needs of priority pollutant standards. To meet this challenge, EPA is developing a series of research contracts leading to analytical methods for these pollutants. A Request for Proposal has been issued calling for as many as 12 contracts covering 114 organic compounds. Each of the contracts is for test procedures based upon similarity in chemical structure and/or predicted instrumental response for a group of compounds.

The contract effort is divided into two phases. Phase I requires the development and evaluation of an interim procedure in the laboratory, based on response to pure standards of the material in a matrix of similar compounds. After the successful completion of this task, Phase II will require testing the method in a minimum of five industrial wastewaters, covering at least five of the SIC codes specified in the Consent Decree. In addition, the contractor will determine the stability of these samples over a seven-day period of holding and prescribe adequate methods for the preservation of the samples. Where possible gas chromatography is to be the primary approach and specific columns and detectors are to be used in the development of the interim methods. At least two dissimilar chromatographic columns must be used.

The contract period is to include 12 months of laboratory and field work, with three additional months for report preparation. The final report must provide complete method descriptions in a standard format, as well as statements of precision and accuracy obtained on the actual wastewater samples examined. The minimum detection limit of the method in the waste samples must also be determined and reported. Contracts are to be awarded by October, 1977, and the final contract product is to be a series of test procedures suitable for routine monitoring of the priority pollutants. The total contract costs are projected to be between $1 million and $2 million.

Experience indicates that the task of developing these methods is formidable. Difficulties with separation of the measured constituent from the interferring matrix can be expected. Instrumental conditions will need to be modified to provide quantitative results. The detection limits and working range desired may be difficult to obtain and the precision and accuracy may be initially unsatisfactory. Additional refinement of the methods will be needed as working experience identifies problems. Since the final proof of success in methods development is the widespread use of the procedure, efforts will be made to provide the methods to interested groups for evaluation prior to any promulgation in the regulations. The method descriptions and supporting data will be forwarded to ASTM and Standard Methods for their consideration as standardized procedures.

In keeping with the policies of EPA, a parallel effort in quality assurance will be carried out. The Quality Assurance Branch of the Environmental Monitoring and Technical Support Laboratory routinely provides reference samples for many of the contaminants included in water supply and wastewater regulations. Standard reference samples for the priority pollutants will be developed to the extent that available resources permit. A series of quality control samples, of known, stabilized concentration, will be prepared and made available to laboratories performing analyses on wastewaters containing the pollutants. A parallel set of performance samples, in the working range of the methods but in concentrations unknown to the analyst, will be developed to evaluate performance capabilities of laboratories conducting analyses on priority pollutants. These samples will be developed through inhouse and contract research and should be available for a significant number of the compounds by 1983. Quality control and performance samples for most of the heavy metals listed in the Consent Decree are already available from the Cincinnati laboratory.

SUMMARY

The setting of standards for priority pollutants requires a major effort in establishing adequate test procedures for the measurement of these substances in environmental samples. The method requirements include approximately 120 elements and compounds many of which are complex organic structures. The hazardous substances occur in a variety of wastes from different industries representing significantly different substrates. The test methods must be specific for the material in the microgram per liter range and must be within the technical and economic capabilities of industrial and governmental laboratories.

EPA is approaching the challenge by means of a series of research contracts for 12 groups of similar compounds, which will provide test procedures for 109 organic contaminants. The total contract effort is expected to cost more than $1.5 million. The preliminary methods should be available for field testing by 1980 and will be promulgated as regulations by 1983.

BIOGRAPHY

Mr. Ballinger is Director of the EPA Environmental Monitoring and Support Laboratories in Cincinnati. Mr. Ballinger holds a B.S. degree in Chemistry from the University of Cincinnati, is the author of many publications in the analytical chemistry of water and wastes. He is a member of the American Chemical Society Water Pollution Control Federation, American Water Works Association, and Research Society of America.

DISCUSSION

Leonard Crame, Texaco, Inc.: When the 1983 EPA toxic tests are developed, what guarantee will we have that the final EPA accepted toxic pollutant test procedures will be consistent with those tests used to develop guidelines?

Ballinger: Those that have been used to define the presence or concentration?

Crame: What assurance do we have that the numbers that will be calculated for guideline purposes will be consistent with what the new test procedures will be?

Ballinger: You'll have absolute assurance that that is the case. In the first place, the contracts now defining BAT are based upon the qualitative aspect. We don't have the problem of identification that we will have in the final. They are also contracts that define the presence of the material and relative concentration. There is no assurance that the specific test procedures will be the same but given the technical constraints of both there are only so many approaches to the determination of an organic compound and they very likely will be consistent, but not exactly. I think, for example, that our final test procedure for monitoring will be perhaps at lower concentrations but require cleaner, better separations and more specific. I think there will be a difference; I hope it is not a significant difference. I don't anticipate any changes in it.

Crame: If it does change anything, will there be a mechanism for changing guidelines?

Ballinger: I don't see how there would be a difference. If for example the standard is based on the concentration in effluents, that standard was developed irrespective of how it is measured. So a measurement technique would not change that if both are specific for the pollutant. It may well be that the analytical method is more sensitive than required. If the standard is not restrictive, that's great; I hope that the standard is not below this sensitivity, then we are in trouble. I don't see the problem if these are not just exactly the same procedures.

Crame: If you use one analytical method now and come up with another in 2 or 3 years from now, will this new method actually be checked against the old method?

Ballinger: They will be checked against the same wastes.

Crame: Right, from our own experience with certain refinery wastewaters even the slightest change in an analytical test will give you significantly higher numbers.

Ballinger: That is true in some measurements, say oil. That's because some measurements are what we call our empirical that the answer you get depends on the method. That's not the case in general with organic structures based on GC or GC/MS. I think in one case we are dealing with what amounts to a definition of the result depending on how you do it. Certainly that's true with what we call oil and grease. I don't think that same case applies when looking at GC/MS.

Ben Buchanan, Phillips Petroleum Company: Will EPA issue or compile the methods after they are developed?

Ballinger: If you mean by an independent method description, yes, EPA intends to publish these methods in our format.

Buchanan: They haven't always been the same method as put out by ASTM and APHA in the past. Are they going to be the same?

Ballinger: We hope so. We will make every effort to get ASTM D19 to adopt the adopt the methods that we have been gathering supporting data on, but they are totally independent groups having a number of independent opinions and we have no control over what D19 does. So it's possible that they will come out with a different method.

Buchanan: The official will be the EPA method?

Ballinger: The official will be the EPA method.

Buchanan: I just wanted to comment that the level of skill required when you get down to parts per billion hasn't been required in the past and that laboratories that are not used to operating down in this area may find it more difficult to get close answers and maybe it might even come to the fact that people with greater skill would have to be employed to do analysis down in this region.

Ballinger: I don't think there's any doubt that when you lower a detection limit or a working range you do require a greater efficiency on the part of the operator, better control over instrument conditions and so on.

Buchanan: In chromatography it's very difficult dealing with interferences as you probably know, and higher molecular weight compounds are more difficult to separate so there may be some real problems with these.

Ballinger: There will be some real problems.

Buchanan: Thank you, sir.

Leo Duffy, Standard Oil Company of Indiana: I took by your comments that perhaps you intend not to use GC/MS in the forthcoming analytical contracts. Is this right?

Ballinger: That is correct. We do not intend to use GC/MS in these contracts if we can get away with it and just use GC, because of the technical and economic factors. A good GC/MS as you know will put you in the $150,000-$200,000 bracket. We consider that not a good approach to routine analyses. So our contracts specifically call bor GC and specifically for certain column and detectors.

F. L. Robertaccio, DuPont: This question does not relate to your topic, but I wanted to ask it anyway. What is your personal opinion of the possibility of laboratory certification?

Ballinger: There are basically no requirements in 92-500 for certification of laboratories. EPA cannot require that data come only from certified laboratories because it is not a part of the legislation. We do feel that the agency has a responsibility for the data that it uses and in decision making therefore anticipate that we will evaluate the laboratories, not certify; judge their data accordingly. Certifying means that we go in and inspect and say the results coming from this laboratory are certified and correct. We do intend to evaluate the laboratories. It is a fine distinction but it is a legal one.

John Hallett, Shell Oil Co: What is being done to evaluate the performance of analytical contractors being used in the refining industry priority pollutant screening and validation surveys?

Ballinger: Right now we do not have the performance samples completely developed for those contracts, but we are working on it right now.

Hallett: Thank you.

Ballinger: However, that is simply an evaluation of EPA's contracts.

METHODS DEVELOPMENT CONTRACTS

LISTED POLLUTANT	NUMBER OF COMPOUNDS IN GROUP
Phthalate Esters	6
Haloethers	7
Chlorinated Hydrocarbons	9
Nitrobenzenes and Isophorone	4
Nitrososamines	3
Dioxin	1
Benzidine	3
Phenols	11
Polynuclear Aromatics	16
Pesticides and PCBs	25
Purgeables (Volatiles)	26
Acrolein, Acrylonitrile, Dichlorofluoromethane	3

"FATES, EFFECTS & TRANSPORT MECHANISMS OF POLLUTANTS IN THE AQUATIC ENVIRONMENT"

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ABSTRACT

Evaluation of environmental effects from exposure to low concentrations of inorganic or organic compounds in the aquatic environment must include a concern for the reactivities and fate of these compounds under natural conditions. At the present time it is not possible to model the detailed fate of many compounds due to lack of accurate information on chemical reactivity and physical transport. However, during the past decade much information has been obtained outlining the general chemical and physical behavior of certain pollutants. Consequently it is possible to make generalized predictions of the fate and extent of persistence of a number of compounds and to point out areas of research to obtain more complete chemical and physical data.

INTRODUCTION

The intent of this report will be to review, in summary form, the fate, transport mechanisms and effects of the important classifications of pollutants of concern for petroleum refinery wastewater. These can be listed broadly as Hydrocarbons, Organics and Metals as indicated in Figure I. For this discussion organics are considered as other than Hydrocarbons. Since Dr. Mount will discuss toxicity testing in the paper immediately following I do not plan to elaborate on the topic of toxicity. For each of the principal classifications a great deal of environmental information has been obtained during the last decade and reported in many diverse publications. However, in only a limited number of these studies are any quantitative results available. Consequently, the information obtained generally provides suggested pathways and recommends research to establish more completely the mechanisms and rate of the processes which exist for the ultimate removal or tranformation to other species which may represent the end product.

HYDROCARBONS

Since the Forum has been called to review wastewaters from petroleum refineries it is appropriate to deal first with the hydrocarbons present as pollutants in aquatic systems. Because of the overall significance much work has been done and reported on hydrocarbon properties and behavior. One report to which reference will be made is from the National Academy of Sciences entitled "Petroleum in the Marine Environment".[21] Another is from the American Institute of Biological Sciences and is the Proceedings of the 1976 Symposium on "Sources, Effects and Sinks of Hydrocarbons in the Aquatic Environment".[2]

A study of high degree of significance to our discussion is that funded by the National Science Foundation - Research Applied to National Needs (RANN) Program on the "Petroleum Industry in the Delaware Estuary" which is currently active.[24] This project is staffed with scientists from Rutgers University and the Philadelphia Academy of Natural Sciences and is engaged in investigating the relative effects of the petroleum industry and other sources in the Delaware Estuary.

The general picture of fates of hydrocarbons in the aquatic system was schematically illustrated by W. D. Garrett[1] in his 1972 publication on the impact of surface films on the properties of the air-sea interface. Figure II taken from this publication is an illustration of the forces which modify hydrocarbon oil slicks on water. Figure II shows, in simplified form, that the forces which operate on oil in water include evaporation, solution, emulsion formation, sedimentation, oxidation, biological assimilation and others. It is important to note that natural, biogenic hydrocarbons, with structures similar to petroleum hydrocarbons are often present in natural systems.[21] The analytical differentiation between biogenic and petroleum hydrocarbons takes considerable effort in many cases.

Volatilization of the lower molecular weight hydrocarbons takes place quite rapidly. This is important because of the toxicity of some of the volatile fractions which are lost soon. Simulated weathering has shown that a crude oil on water loses essentially all components boiling below C_{12} within 24 hours in the laboratory.[3] It has been observed that the toxicity of a crude oil mixed with water was greatly reduced even by short weathering.[4]

Solution. Evaporation and solution both act most strongly on the low-molecular weight hydrocarbons. The true solubility of hydrocarbons drops exponentially as a function of their molecular volume.[5] Consequently, although toluene is soluble in water to 515 ppm, anthracene is soluble to less than 0.1 ppm. The higher polynuclear aromatics are considerably less soluble.

Oxidation. This is a selective process and can be subdivided into chemical oxidation and photooxidation. Absorption of photons by the heavier aromatics with suitable spectral properties will initiate the reaction chain leading to conversion of these materials. Products of the reaction will contain oxygen and could consist of phenols, carboxylic acids, alcohols and the like. Since these are more water soluble than the hydrocarbons, they will be more completely lost to the water column leading to greater dispersion.

Microbial degradation. This subject has been studied over many years by many competent investigators. They conclude[7,8,9,10] that microorganisms which oxidize various hydrocarbons are widely distributed in soil and water, especially in estuaries and shorelines. Although normal paraffins are most susceptible, virtually all hydrocarbons are degraded including aromatic hydrocarbons of condensed structures. These bacteria, which use hydrocarbons for an energy source, are effective in converting hydrocarbons to carbon dioxide and water. Probably one of the major ways in which hydrocarbons are removed in estuaries and coastal areas is by microbiological degradation. For example, Zobell[7] reported that in coastal areas bacteria can oxidize from 0.02 to 2 grams of hydrocarbon per square meter per day depending on several factors including rate of oxygen diffusion. In shallow waters this approaches conversion rates on the order of a part per million of hydrocarbon per day. It is important to realize that bacteria are active even in very cold arctic water.[11,12]

Biochemical uptake metabolisms and discharge of hydrocarbons. It has been shown that marine organisms, maintained in water containing oil, take up hydrocarbons in their tissues. Following a spill of No. 2 fuel oil near West Falmouth, Massachusetts in September, 1969, Blumer[13,14,15] analyzed oysters, scallops, and other marine organisms and found that they had taken up oil fractions. He kept three oysters in flowing sea water in his laboratory. One oyster was analyzed after it had been kept in flowing sea water for 72 days and the other two after 180 days. His publication in 1970[14] stated that none of these three oysters had purged themselves of the oil they contained prior to the beginning of the experiment. He concluded "Thus, once contaminated, shellfish cannot cleanse themselves of oil pollution".[14]

A number of scientists have reinvestigated this matter and have shown that marine animals do indeed take up hydrocarbons but actually do cleanse themselves. Experiments have been done with, literally, hundreds of aquatic animals. Data now in hand clearly show that aquatic animals do take up hydrocarbons but that, when the animals are placed in clean water, the hydrocarbons are purged or metabolized. For example, Lee and his co-workers[16,17] described the uptake, metabolism and discharge of radio-labeled aromatic hydrocarbons by mussels and by fish. They found that these compounds did indeed find their way from sea water into the aquatic animal tissues, but that when the animals were placed in clean water, the hydrocarbons were lost. The mussels purged the hydrocarbons unchanged whereas the fish metabolized these products. In another study, Anderson[18] carried out exposure tests on oysters and clams, illustrated in Figure III taken from his work. In these tests, oysters were initially exposed to a highly aromatic fuel oil. The animals were then placed in clean sea water. Specific analyses for individual hydrocarbons were made and purging was found to the level of analytical sensitivity. Very similar data have now been found in studies at other locations in the United States including Battelle-Northwest in the State of Washington[19] and more recent data from Woods Hole[20] using, in each case, local animals. In every case examined, purging was found to occur.

The National Academy of Science Report[21] states: "organisms such as mussels and oysters have been shown to eliminate most absorbed petroleum hydrocarbons when placed in clean water".

Accumulation in the food web. The additional question of accumulation of petroleum hydrocarbons in the food chain should be considered. Lee's results[16,17] show a rapid metabolism of certain aromatic hydrocarbons in fish. Data from Anderson and others show relatively rapid purging of hydrocarbons from animals placed in a clean environment. Once the animal is no longer subjected to water contaminated with oil, the affected organism cleanses itself quickly of whatever oil contamination that it may have incurred. Therefore, it is not likely that such contamination would become concentrated by transfer from one trophic level to the next through the food chain. In fact, the National Academy Report[21] states "There is no evidence for food-web magnification of petroleum hydrocarbons in marine organisms."

Significance of Field Studies. Field studies have been conducted principally in regions where oil and gas production has taken place.[45,46] These have all shown that neither oil spills nor continued production have detrimental effects on the environment. Grossling of the U. S. Geological Survey reported[44] that, even in areas of extremely massive oil spills of some years ago, there are "no Death Valleys". Natural forces which degrade oil have taken over and converted the spilled oil into the end products of nature, carbon dioxide and water. Reviews of current producing areas have shown no detrimental effects.[45,46] Detailed chemical and biological surveys of producing area and a control area in the Gulf of Mexico shows that production of petroleum had no discernable effect on the environment.[45] The underwater surveys[46] of Platforms "Hilda" and "Hazel" in the Santa Barbara Channel have demonstrated much increased marine biota in and around the platforms. Studies of the petroleum industry in the Delaware Estuary[24,47] have shown that the city of Philadelphia and its environs contribute much more "oil and grease" than does the refining industry in the area. Contributions of "oil and grease" from the metropolitan area are larger from drains and storm-water runoff than from the refining sources.

POLYNUCLEAR AROMATICS HYDROCARBONS (PAH)

Because of the concern for the presence of some carcinogenic polynuclear aromatic hydrocarbons (PAH) in the aquatic environmental this subject is worthy of separate discussion. It must be pointed out that only a limited number of PAHs are carcinogenic. Those that are carcinogenic will contain 4, 5 or 6 rings. Only certain isomers are carcinogenic; for instance benzo(a)-pyrene is carcinogenic but not its isomers.[42] Considerable data are now available from a number of sources[21,23] which show that polynuclear aromatics are widely distributed in soils at very low concentrations and may have occurred on the earth's surface during geologic time. Presumably a source of PAHs has been from combustion such as forest fires or in more recent times, from burning of coal.

Microbial degradation. Biological degradation of polynuclear hydrocarbons has been discussed by Professor Gibson at the Symposium on Sources, Effects & Sinks of Hydrocarbons in the Aquatic Environment.[2] He pointed out that, since aromatic hydrocarbons have been ubiquitously distributed throughout the environment over geologic time, living organisms have evolved enzyme systems which oxidize these compounds. Table I, taken from his publication[25] shows the types of aromatic hydrocarbons known to be susceptible to microbial oxidation. One common feature of the mechanisms used by bacteria to degrade these types of compounds is the introduction of hydroxyl groups. Generally, two hydroxyl groups are introduced and the diol so produced is then subjected to further degradation. A metabolic pathway for the complete degradation of naphthalene is indicated in Figure IV. The compounds shown in brackets have been completely identified. The end products of this mechanism are the non-toxic products, carbon dioxide and water.

Less is known about the detailed chemistry of microbial degradation of PAHs that contain three or more rings. However, evidence is being obtained that bacteria are capable of oxidizing aromatic hydrocarbons that range in size from benzene to benzo(a)pyrene. A mutant strain of bacteria, *beijerinckia*

B836 has been shown to oxidize biphenyl,[26] phenanthrene,[27] and anthracene[28] to dihydroxydiols. Benzo(a)pyrene was oxidized by this bacteria to dihydroxy product as shown in Figure V, as well as to other products resulting from further degradation.[29]

Biochemical uptake and discharge. Because of the specific concern for the PAHs, investigators have repeated uptake and purging studies with individual PAHs and find results identical to that found with other hydrocarbons. That is, aquatic animals will take up PAHs in their gut and their tissues, and that these are purged or metabolized when the animals are placed in clean water. Recent work of this nature has been conducted by Neff[39] and Neff and Anderson.[40] The conclusions of these studies were that the pattern of uptake and depuration of benzo(a)pyrene in the clam is much the same as observed earlier from the naphthalenes. Benzo(a)pyrene appears to be accumulated more rapidly, however, and released more slowly than the naphthalenes. In their experiments purging was a consistent process, declining to a level of only 1.4 percent of the accumulated material in 20 days. Benzo(a)pyrene could not be detected in clams maintained in isotope-free sea water for 58 days (limit of detection 0.01 ppm). It is interesting that the viscera contained most of the activity at all sampling periods.

Photochemical oxidation. Since the polynuclear aromatic hydrocarbons have high absorptivities in the ultraviolet, it is likely that photochemical oxidation plays an appreciable role in their degradation. In fact a review states that photooxidation is probably one of the most important processes in removal of polycyclic hydrocarbons from the atmosphere.[42]

ORGANICS

Many of the same factors which operate to dispose or degrade hydrocarbons are also effective on many organics, depending of course on properties of the individual compounds. Such factors as volatilization, solution, sedimentation and oxidation are likely candidates for removal or transformation and should be studied. It is well known that ethers are easily oxidized and it is likely that this is the mechanism of their loss in a natural system. Oxidation is also possibly the route for the loss of other relatively reactive organic compounds. Because of the reactivity of organic functional groups other reactions such as hydrolysis, reduction and dechlorination may be important.[48]

Photochemical. Photochemical energy reaches us from the sun in the form of photons with wave lengths covering the spectra from infrared to the far ultraviolet and including the visible. In fact, all the solar energy we receive is in the cumulative energy of the photons which fall upon the earth. Photosynthesis is our most important photochemical process, without which there could be no life on earth since plant growth depends upon the photochemical conversion of atmospheric carbon dioxide into organic substances. The significance of photochemical processes is becoming more and more apparent in the environmental chemistry of organic materials. The photochemical oxidation and dechlorination of a number of the highly chlorinated pesticides and similar compounds has been well established. A particularly significant recent paper appeared in "Science" last March indicating that the toxic, complex substance TCDD (2,3,7,8 tetrachlorodibenzo-p-dioxin) is photochemically degraded by sunlight[6] in the natural environment. Presumably the degradation reactions involve dechlorination and perhaps oxidation. Photo sensitived oxidations may also play a significant role in the observed degradation of DDT in the environment[30] as well as with other pesticides.[48]

Microbial degradation. The microbiological metabolism of organics has been the subject of detailed study for a number of years and has been extensively reported.[31,32] Investigations similar to those outlined above for polynuclear aromatics have been reported on phenols (Dagley, University of Minnesota),[32] on surface-active agents (Huddleston and Allred, Continental Oil Co.),[32] on insecticides (Matsumura and Boush, University of Wisconsin)[32] and on other classes of commercial organic compounds that could be present in waste waters. A number of bacteria widely distributed in nature, have the ability to degrade phenolic compounds. The ability to degrade phenolics is not confined to bacteria. These reactions take place also with fungi and in species of *aspergillus*, *penicillium* and *oospora*. The end products of these conversions are simple, essentially non-toxic organic structures.

Organic halogen compounds have been shown to undergo a number of microbiological reactions which result in loss of halogen and its replacement either by hydroxyl or hydrogen. Microbiological hydrolytic dehalogenation is the most common reaction. These reactions seem quite general in natural soils. Some examples which have been documented[49] include *lindane* which undergoes microbial decomposition under anaerobic conditions to release chloride ion and the *brominated derivatives* of ethane, propane and butane which produce either the simple hydrocarbons or alcohols upon loss of halogen. Aliphatic halides such as allyl chloride and 1,3-dichloropropene hydrolyze readily in the soil.

Edwards[50] points out that insecticides in soils are largely broken down by microorganisms. Some of molds indicated above to be able to utilize phenolics are also effective in converting chlordane and heptachlor into hydrophilic degradation products. Several soil bacterial species have been found able to dechlorinate lindane.

Biochemical uptake and metabolism. It is well known that aquatic species concentrate organochlorine insecticides[33] but is is perhaps not as well recognized that there is also an appreciable amount of degradation by the living species. Johnson, Saunders, Sanders and Campbell[33] used radiochemically-labeled aldrin and DDT in studies with freshwater invertibrates and found, in 3-day exposures, that some degree of degradation of aldrin and DDT occurred with all organisms examined in the limited time of the tests.

It is interesting that natural products containing bound halogen are produced by aquatic biota. Dr. Faulkner of Scripps presented a paper at the Symposium on Sources, Effects & Sinks of Hydrocarbons in the Aquatic Environment[2] which described a group of halogen-containing terpenes biogenically synthesized by aquatic organisms.

Significance of field observations. There are many natural reactions which degrade organic compounds, including organic pesticides, which have now been documented from field and laboratory observations. As a result of these reactions it has been stated that "there are no permanent organic pesticides".[48] Degradation apparently continues onto the non-toxic inorganic products with rates depending upon many factors, such as climate, temperatures, soil type and so on.

METALS

To put a perspective on the effects of metal ions in the aquatic environment it is useful to turn to an important concept introduced by Dr. Ketchum of Woods Hole. This is the Relative Critical Index as described in Table II. This Table lists toxic elements considered to be of critical importance to aquatic pollution. The "toxicities" (concentrations in μg/l) assigned to the metals in the table are in a decreasing order of toxicity, and each "toxicity" concentration quoted is considerably smaller than the concentration acutely toxic to man or the aquatic environment. These toxicity values are obtained from "Water Quality Criteria".[41]

The concept of Relative Critical Index in Table II is derived by Ketchum[34] by dividing the annual amount of a substance mobilized by human or natural activities by the assumed "toxicity". This index helps to identify elements as pollutants and assists in establishing the relative contributions of trace elements from nature and from man-made sources. For instance, it can be seen that the greatest input of most trace metals listed is from natural sources. Where the natural contribution is a large portion of the potential supply, control of individual sources whose concentration levels are low would have little effect on water quality.

Chelation. There is an increasing body of evidence indicating that there are natural processes operating to reduce both the concentration and toxicity of trace metals dissolved in water. In most natural waters much of the free metals ions would probably be bound to organic substances naturally present in the water. There is evidence that organically chelated heavy metals in aqueous solutions do not have as great an effect upon organisms as do solutions of the metal salts.[35,36] This could be due either to the fact that the organometallic complex is to bulky to enter a biological system or it could be due to the lack of availability of the metal ion for reaction with enzymes within the cells.

Reduction. Methylation of mercury in the aquatic environment can be caused by the reductive action of anaerobic bacteria at the bottom-water interface.[51] These bacteria produce the highly toxic dimethylmercury $(CH_3)_2Hg$ and methylmercury CH_3Hg^+. It was this type of mercury pollution which was the cause of the notorious "Minamata disease" in Japan in 1953.[52]

Sedimentation. Detailed metal analysis of sediments and benthic marine populations have been conducted near sewage outfalls in the Pacific Ocean off the Southern California Coast.[37] No significant differences were observed for sole caught in polluted and unpolluted areas for the following trace elements, mercury, cadmium, copper, zinc, iron and cobalt in the sediments. In the reported discussion which followed the above presentation[37] it was stated that similar results were found in England. The suggestion was made that sediments may be a useful final sink for many metals and that the adsorption of the metal ions to the surface of sediments precludes their uptake by biological systems. I would suggest that an important research study would be that of evaluating the biological availability or nonavailability of sediment-associated metals in the aquatic environment.

Essential nutrients. Almost any element or substance can be toxic to plants when present in abnormally high concentrations. Yet many toxic elements have been shown to be essential nutrients at low concentrations, at least to certain plant species.[38,43] Drake of the University of Massachusetts lists[43] as essential micronutrients the following: iron, manganese, copper, zinc, boron, molybdenum and chlorine. It has been recognized especially by orchard growers that essential elements must be introduced when soils are deficient. Consequently "zinc nails" are sometimes driven into trees when soils are deficient. Enzyme system in plants seem to require manganese, iron, and molybdenum as well as magnesium in trace amounts. There is apparently some evidence that selenium may be a necessary trace nutrient to some plants.[38]

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BIOGRAPHY

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Figure I

SCHEMATIC REVIEW OF PRINCIPAL FATES, EFFECTS AND TRANSPORT MECHANISMS OF POLLUTANTS IN THE AQUATIC ENVIRONMENT

	Hydrocarbons	Organics	Metals
Fates	Volatilization Solution Sedimentation Oxidation	Volatilization Solution Sedimentation Oxidation Photochemical Dechlorination	Chelation Oxidation/Reduction Sedimentation
Transport Mechanisms	Air-Water Interface Sediment Transport	Air-Water Interface Sediment Transport	Sediment Transport
Effects	Oxygen Consumption Biological Assimilation Toxicity	Oxygen Consumption Biological Assimilation Toxicity	Biological Assimilation Essential Trace Elements Toxicity

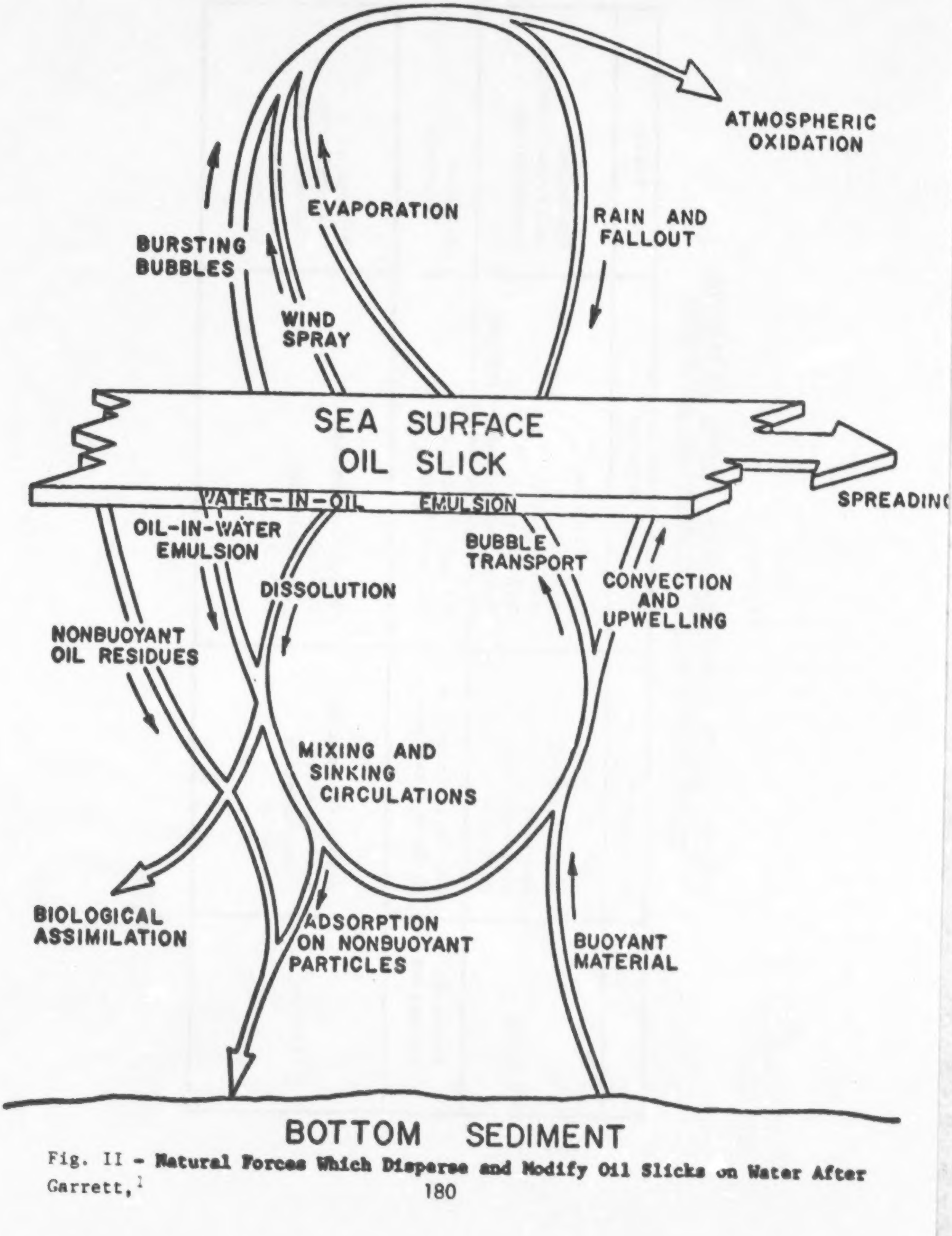

Fig. II - **Natural Forces Which Disperse and Modify Oil Slicks on Water After** Garrett,[1]

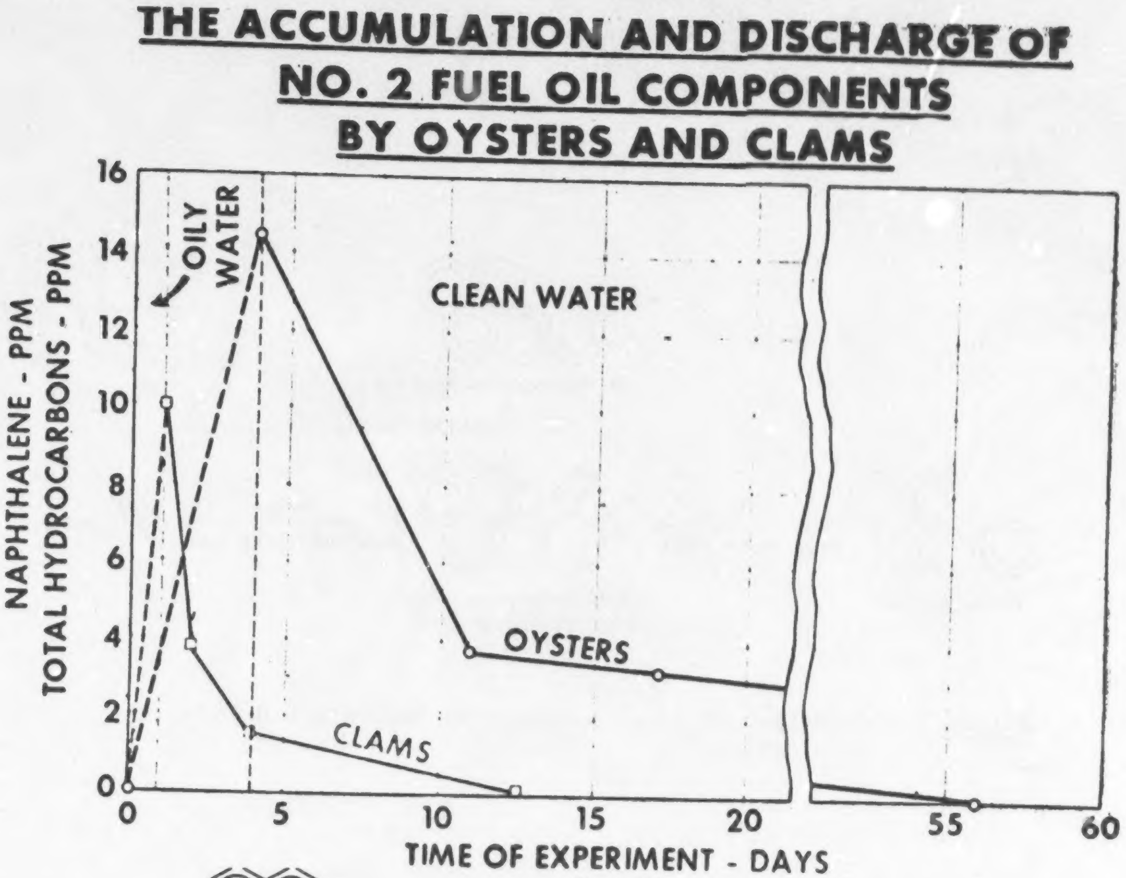

Figure III

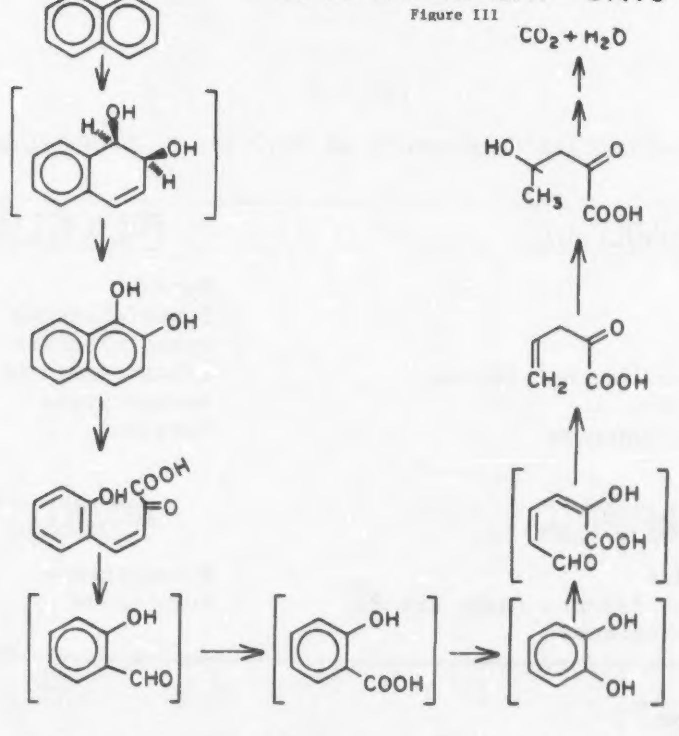

Figure IV Metabolic Pathway for the Degradation of Naphthalene by Certain *Pseudomonas* Species. From Gibson[25]

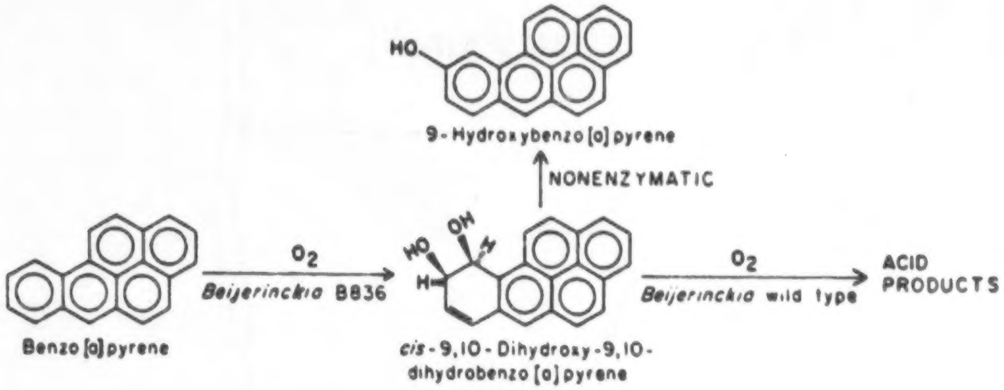

Figure V Oxidation of Benzo(a)pyrene by *Beijerinckia* B836. From Gibson[25]

Table I

AROMATIC HYDROCARBONS KNOWN TO BE OXIDIZED BY MICROORGANISMS[a)]

MONOCYCLIC

- Benzene
- Toluene
- Xylenes
- Tri and tetramethylbenzenes
- Alkylbenzenes
- Cycloalkylbenzenes

POLYCYCLIC

- Pyrene
- Benzo(a)pyrene
- Benzo(a)anthracene
- Dibenzo(a)anthracene
- Benzperylene
- Perylene

DICYCLIC

- Naphthalene
- Methylnaphthalenes (mono and di)
- Ethylnaphthalenes

TRICYCLIC

- Phenanthrene
- Anthracene

a) From Gibson[25]

Table II

METAL TOXICITY AND RELATIONSHIP TO INPUT[34]

ELEMENT	TOXICITY µg/1	RATE OF MOBILIZATION (10^9 G/YR) A(MAN)	B(NATURAL)	C TOTAL	RELATIVE CRITICAL INDEX,* 10^{12} 1/YR MAN	NATURE
MERCURY	0.1	1.6	2.5	4.1	16,000	25,000
CADMIUM	0.2	0.350	2.65	3.0	1,750	13,250
SILVER	1	0.07	11	11.1	70	11,000
NICKEL	2	3.7	160	164	1,350	80,000
SELENIUM	5	0.45	7.2	7.7	90	1,440
LEAD	10	3.6	110	113.6	360	11,000
COPPER	10	2.1	250	252.1	210	25,000
CHROMIUM	10	1.5	200	201.5	150	20,000
ARSENIC	10	0.7	72	72.7	70	7,200
ZINC	20	7	720	727	70	36,000
MANGANESE	20	7.0	250	257	330	12,500

*RELATIVE CRITICAL INDEX = $\frac{\text{INPUT}}{\text{TOXICITY}}$

WEISS PAPER DISCUSSION

Paul Mikolaj, Lion Oil Co.: Do you have any idea of how the information you have presented will be used in the setting of the standards for the priority of pollutants?

Weiss: I would hope that the answer is yes. If anybody cares to answer that from the floor I would like to hear an answer.

Ridgeway Hall, EPA: I think without a doubt if information of that type is timely submitted to EPA in the course of the rule-making proceedings, we certainly will consider it.

Ridgeway Hall, EPA: On your chart of Table II which you last had up there, could you tell us what the significance of the right-hand column was and how those numbers were derived and what they mean?

Weiss: That is actually the relative critical index itself. These columns come from taking the toxicity and dividing the toxicity into the rate of mobilization to develop a ratio. What it means is that the ratio indicates the relative significance of the element to toxicity.

D. I. Mount, EPA, Duluth: In regard to Table II that you have on the board I think it is a useful table but I think it is also important to point out that it makes no account of the form in which those metals are being transported or converted by man and by nature. For example, in the case of mercury most of the natural mercury is transported in the mineral form or in sulfide forms that are insoluble. In the case of much of the man-transported mercury, it is in vapor form in power plant stacks so that the biological significance in a given amount of that metal will make it quite different, even the total quantities show a different picture.

George J. Putnicki, UTD: Are there any taste and odor studies conducted concurrently with the concentrations of the number of two fuel oil?

Weiss: We did not conduct any taste or odor studies. There are independent studies which have been done on taste and they show depuration. The oyster farmers in Louisiana find it is about the same order of time, three or four weeks. When they observe contaminated oysters, they put them into a clean bed, so the timing is the same but they were not done concurrently.

MEASURING AQUATIC IMPACT OF TOXIC CONTAMINANTS

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The impact of toxic pollutants on aquatic systems is often a principal concern about the manufacture and use of chemicals, that may be discharged or otherwise released into the environment. Our system of streams and lakes seems to function in much the same way as the lymphatic system in our bodies--collecting what "seeps through" as a result of our industrialized society that liberally employs synthetic chemicals in its day-to-day operations. Whether toxic chemicals are put in landfills, discharged in liquid effluents, incinerated, or lost to the air through vaporization, we should not be surprised to find them in our rivers and lakes. If toxic and persistent enough, we can expect them to cause problems, either from direct effects on the environment or through residues in organisms. We have also learned, that pollutants may be drastically altered in their chemical form or biological behavior once released into the complex environment of streams and lakes.

The local area of release is not the only one of concern. We may well find effects of pollutants occurring far downstream or even in our coastal waters without any discernible effect in the immediate area of discharge.

The responsibility of these chemicals after discharge, no matter how geographically remote or how long after the release has been made, must become a way of life and a part of doing business. The alternative under which we have been living in the past places the burden of remedial measures on those who did not cause the problem. It is encouraging to see that many companies are as concerned about the consequences of the chemicals in their wastes as are the regulatory agencies, and I am sure that this concern will lead to a lessening of the crises that we have faced in the past few years. Undoubtedly, with modern analytical methods and our considerably improved knowledge of aquatic systems, the apparent increase in problem chemicals may well be one of better identification rather than an increase in problems.

For all of these reasons, and perhaps for many others, there is a mounting concern and effort to develop more rapid, reliable and cheaper methods for predicting the impact of toxic chemicals on the aquatic environment and before they become problems. The passage of the Toxic Substances Control Act undoubtedly was hastened by these same problems and concerns. Since the emphasis in that act is one of properly testing chemicals before they are used and before they become a problem, the need for rapid, predictive tests has been even further strengthened. If indeed that is the thrust of the regulations which will be developed, then it is obvious that most of the predictive toxicology work will have to be done in the laboratory and field studies will be relegated by and large to an assessment of the accuracy of decisions made during the pre-market testing period.

The testing of single chemicals under the Toxic Substances Control Act and the assessment of toxicity from petroleum refinery wastewater have one thing in common. The variety of pollutants and mixtures in both is so large that what can be done on any one chemical or any one waste will have to be quick and relatively inexpensive.

Petroleum refinery wastewater has posed difficult problems to those trying to develop acceptable waste treatment systems to adequately remove the toxic chemicals contained in it. These wastes contain chemicals that are water insoluble but fat soluble, and these are the very ones which most often cause residue problems in organisms and are often of the highest toxicity. Unfortunately, one cannot find "reagent grade" petroleum refinery wastewater on which to do his experiments and make predictions, so the problems associated with these wastes are compounded as compared to the ones associated with pure, single chemicals.

At this point, it would be well to discuss the significance of some specific toxic effects which have received much attention in the past few years. I refer particularly to carcinogenicity, as well as teratogenicity and mutagenicity. There are two problem areas in which these effects should be considered in assessing aquatic impact. One area is the induction of any one of these toxic effects in aquatic populations with resultant population effects. In such cases, we must recognize that these effects are no more significant than many other effects such as reduction in growth rate, mortality, or reduced reproductive rates, to the populations of concern. It makes no difference to society whether aquatic organisms are killed by malignant tumors or by avoidance to a particular material in a water body. In either case, it is a decimating factor on the population, but no particular importance is attached to the effect because it is due to cancer. On the contrary more emotional importance is attached to human suffering from cancer than to suffering from an automobile accident. Therefore, carcinogenic, mutagenic, and teratogenic properties have no special significance for aquatic organisms. If, however, aquatic organisms accumulate chemicals with these properties and thereby increase the exposure of human populations to such chemicals, then we must have special concern.

No useful purpose would be served by listing all of the tests that are now available for assessing impact on aquatic systems in a paper such as this one. Great progress has been made in the last fifteen years in developing more refined and sophisticated tests to measure the toxicity of chemicals to aquatic systems. Indeed, the state of the art as it is practiced in aquatic laboratories probably approaches the quality of that used in mammalian toxicology laboratories and standard protocols for conducting aquatic toxicity tests are easy to find and comparable to those for mammals. The problems in mammalian toxicology and aquatic toxicology are all generically the same and revolve around appropriate test organisms for prediction of effects, quality of test animals, length of exposure, effects measured, and laboratory quality control. One who needs to test aquatic impact now has available to him a selection of test organisms (U.S.EPA 1975) which have been successfully employed in laboratory testing. There are at least fifteen or twenty aquatic organisms ranging from fish to protozoans and algae that have been successfully cultured in laboratories and are adaptable to test conditions in aquatic testing systems. While some of these species may not be particularly important in themselves in aquatic systems, such as for example, Daphnia magna, the data base concerning the sensitivity of such organisms to a variety of chemicals strongly suggests that they are not overly sensitive and that they can be used as the "white rat" for predicting effects on other organisms.

The data base on toxicity of chemicals to aquatic organisms is now reaching proportions large enough so that some reasonable judgments can be made in the selection of the most appropriate test organisms. Especially with single chemicals produced for particular purposes, often the objective in producing the chemical leads one to the selection of the proper organism. Obviously, if the chemical is produced for use as a herbicide, it only makes good sense to test its effects on plants such as algae or macrophytes. Likewise, chemicals designed to kill insects should be tested on aquatic arthropods and preferably aquatic insects. This is not to suggest that a variety of organisms should not be tested where possible, but since time and funds are nearly always limiting, the bulk of the effort available can be expended on what are likely to be the more sensitive organisms.

For a variety of aquatic species, there are now acute and chronic test methods available which enable one to measure effects ranging from short term, LC50 measurements to very sophisticated and sensitive life cycle tests (U.S. EPA, 1973; U.S. EPA, 1976; Woelke, 1972; APHA, 1975). In chronic tests, one can examine the effects of a toxicant on all life stages of the organism and measure effects on reproduction and progeny growth as well as effects such as malformations. There are now approximately 100 chronic tests with several fish species on perhaps 50 to 75 different toxic materials. An examination of this data base reveals that one can be reasonably accurate for most chemicals by looking at segments of the life history in toxicity tests and avoid the expensive chronic tests for full life cycles (McKim, 1977 and Macek, 1977). These authors point out that if one measures the toxic effects on the eggs and larvae of fish, he will find as the no-effect concentration one that is not greatly different from the one that would be found if the animals were exposed throughout their life history beginning with eggs and ending with growth data on the F_1 progeny. Other studies have revealed that the gill-cleaning reflex commonly called the "cough response" is a highly reliable indicator of the concentrations which will or will not have chronic effects in a life history exposure for fish (Spoor, et al., 1971· Drummond,

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et al., 1973 and Drummond, 1974). Through the use of both models and in a different approach by using resin columns (Neely, et al., 1974; Chiou, et al., 1977 and Veith, 1976) bioconcentration properties of chemicals can be rather accurately predicted from either very short tests with organisms or through a strictly chemical, analytical approach. Indeed sufficient correlations exist now to enable us to be reasonably certain that the single chemical property of the partition coefficient (between octanol and water) is a reliable predictor of whether or not one can expect the chemical to bioaccumulate.

Species of fish are now available that make possible chronic life history tests in a matter of two months or less (Smith, 1973) and tests with Daphnia and some of the aquatic insects are now fully developed and can be expected to produce reliable results in an acceptable period of time. The cost of doing tests such as described above is certainly acceptably competitive with other analyses that are now required on chemicals and the insertion of biological tests into requirements for evaluating chemicals is becoming a matter of routine. Physiological and biochemical tests on fish in particular and other tests on invertebrates, have yet to find a promin[illegible]place in assessing the effects of toxicants on aquatic organisms. Perhaps this is [illegible]esult of the unregulated body chemistry which is so typical of most of the aquatic poikilotherms.

It seems quite fair to say that the ability to measure aquatic toxicity and expected toxic effects on aquatic populations is substantially more advanced than is our ability to predict the behavior of chemicals in the environment. The metabolic pathways, the transport of these chemicals from area to area, and perhaps most important of all, the permanency of the apparent sinks such as the sediment in lakes, seem the most difficult judgments to make when assessing environmental impact. Estimating what concentrations will occur as a result of expected production and usage rates and how the chemicals will get there, where they will go and how long they will stay before they are degraded into something else, is not routine.

This leads me to express a word of caution about the confusion which can exist regarding the distinction between toxicity and hazard. In our rush to assure that highly toxic chemicals are not released into the environment, there is a danger that we will reject a chemical because it has a high toxicity and a low hazard in favor of another chemical which has a much lower toxicity but a higher hazard. Our systems, both aquatic and terrestrial, have lived, evolved and thrived in the presence of some very highly toxic substances. Ozone rates very high on the list of toxic materials, and yet its persistence in the environment is so short that it is not a problem. Too often, I'm afraid, demonstrated high toxicity casts the dye before an assessment has been made as to whether or not the chemical is going to be an environmental hazard. Experience has taught us that the chemicals to be most concerned about are those which are persistent and are nearly water insoluble but highly fat soluble. These are the ones which last for a long time in the environment and accumulate in the bodies of aquatic organisms. They too are the ones that are likely to form unacceptable residues in those organisms used for human consumption. During the last five years, this category includes most of the emergencies that have arisen on the Great Lakes, the James River, and elsewhere in the country.

With the widespread use of rapid tests, a danger exists that we will stop developing better methods that are both quicker and more accurate. An even greater danger is that we will discontinue the development of chronic toxicity data and other information which is so vital to understanding how chemicals affect aquatic systems. It has only been through the development of an extensive chronic toxicity data base that the validity of many of these short-cut methods, now available, could be evaluated. Unless we continue to advance the basic science of aquatic toxicology, the return on future efforts to develop better methods and make better predictions will be lessened. We have an urgent need to see that a proper balance occurs between funds expended for the development of laundry lists of numbers for making regulatory decisions and, on the other hand, the advancement of the basic science of aquatic toxicology. We need better understanding of modes of action and further work on selection of the most appropriate organisms on which to perform our tests. Neither can we forget that our ultimate goal is to protect a system which is not a random collection of individuals, but rather a relatively intricate grouping of plant and animal populations which are interdependent on each other and which will all be affected by a change in any one. Sometimes one gets the impression that those working on aquatic ecosystems think that there is a universal aquatic ecosystem which, if understood, could explain all other systems. Certainly such is not the case, but indeed most workers do expect that the general functions that occur in aquatic systems are similar enough that once the fundamental ones are understood, data from laboratory experiments such as the toxicity tests described above can be more intelligently and efficiently applied to the problems of the real world.

The increasing scarcity of natural resources and the attendant rise in cost for these materials will probably force us to use a property of ecosystems which we have tried not to use in the past decade. I refer, to the assimilative capacity of waters which can be so useful to us, but which has been so abused during the first three quarters of this century. Because we so foolishly abused that valuable resource of aquatic systems in the past does not in any way preclude the intelligent use of it in the future. As man becomes smarter about the total ecological effect of his activities which satisfy his seemingly infinite desire for contraptions, we may recognize that the mountains of sludge that we produce in our chemical waste treatment plants and the attendant environmental damage and resource drain that accompanies the mining, production, transportation and application of these chemicals, may well create a far more serious ecological effect than the intelligent utilization of the assimilative capacity. If one takes an old fashioned and true ecology course, one of the first principals he learns is that the environment affects all organisms and all organisms affect the environment. Man is an organism. He has, does now, and always will affect the environment in which he lives, and our goal must be to affect the environment in the least adverse way. I am convinced that it would be easy for us in our efforts to avoid aquatic impact "at any price" to produce a far greater ecological impact on the total system, that is more undesirable from man's point of view--all because we made a mistake in the past by expecting the impossible from our aquatic systems.

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DISCUSSION

L. Duffy, Standard Oil of Indiana: With the demands and problems of the analysis of the problem organics, do you view bio-assay as a better analytical tool?

Mount: Yes. The only valid way to measure toxicity is with an organism. You can't do it with an analytical instrument and yet we seem to rely on the analytical approach with no regard for biological response even though that really is the goal toward which much of this work is aimed. I think that the toxicity test or the bio-assay should be considered as an analytical tool and that it can do much to reduce the costs of doing complex analytical work. Also, the high pressure liquid chromatographic column, for example, might separate away 90% of the compounds in a waste or a mixture of materials that we are not all that concerned about and help us zero in on those which are going to be problems.

Paul Mikolaj, Lion Oil Company: What is the state of the art in the future of continuous-flow bio-assays?

Mount: The chronic test that I mentioned must be done in a continuous flow system and as I said, I think it must remain the foundation of our aquatic toxicity work, but it doesn't have to be a routine workhorse. It is through chronic tests, analagous to the two-year rat study which is so common in other toxicology work, that you find the mode of toxicity. Such information is necessary for rapid test development and predictive toxicology. So I see the chronic test as being the workhorse in the research laboratory, so to speak, where one develops the fundamental toxicology to evaluate the suitability of much faster methods. In the prepared paper I have pleaded for a proper balance between the effort that goes on fundamental research and developing numbers in a production laboratory. The chronic test is an extremely essential tool as a fundamental test and of course, depending on what problems you are trying to mimic in the real world, it may be very useful for other purposes. If one is concerned about a relatively continuous discharge, then obviously the flow-through system is the way to go. If one is concerned about a pesticide application, then the exposure period is likely to be short, and then perhaps it is not the right test. I think we should be careful that we don't confuse continuous flow with continuous exposure, because they are different tests.

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Donald I. Mount holds a B.S. degree in Wildlife Conservation from Ohio State University. He also earned a M.S. and a Ph.D. from Ohio State University, concentrating on fish toxicology and physiology. He is currently Director of the Environmental Protection Agency Research Laboratory-Duluth, Minnesota. Dr. Mount has served on various national and federal committees in the interest of water quality control. He has also published over 40 articles.

AN OVERVIEW OF ADVANCED TREATMENT SYSTEMS

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The term "advanced treatment systems" can have many connotations, ranging from what is generally considered a 1977 level of technology (Best Practicable Control Technology Currently Available) to Best Available Treatment Economically Available required by 1983, or some level in between. Translating these levels of technology into unit process requirements, the systems discussed in this overview include biological treatment, biologically-treated effluent polishing, and physical-chemical treatment, primarily related to petroleum refining, petrochemical, and organic chemical wastewaters. Recent developments relative to process optimization and limitations will be included, as well as documentation of process performance.

BIOLOGICAL TREATMENT

Although biological treatment systems per se are normally not considered "advanced," they do serve as the most important component of most treatment facilities which either now or in the future must produce effluents with a quality consistent with advanced wastewater technology. The trend during the past decade has been toward the use of high rate biological processes for the treatment of organic industrial wastewaters. The systems have generally included either suspended-growth (activated sludge) or fixed-growth (rotating biological surface) processes or some modifications thereof. The completely mixed activated sludge process is the most widely applied biological system in treating industrial wastewaters with relatively high organic concentrations. The problem most common with activated sludge systems treating industrial wastes is accomplishing effective solids-liquids separation in the gravity clarifier which follows the aeration basin. Many industrial wastewaters will tend to generate a significant fraction of dispersed biomass which do not adequately separate in the clarifier. For example, the average effluent suspended solids (TSS) will range from 25 to 75 mg/l from an activated sludge process. If the effluent limitations are more restrictive than the indicated range, then effective effluent polishing systems must be included in the process design, such as the ability to add organic polymer flocculants and/or granular media filtration.

More recently, fixed-growth systems are becoming quite popular in the petroleum refining and petrochemical industrial categories (Ref. 1). One of the more popular fixed-growth systems is known as the rotating biological surface (RBS). In this system the biological mass grows on the surface of large-diameter discs which are placed side by side on a rotating shaft. The bottom portion of the rotating discs are emersed in a basin through which the wastewater flows. It is a facultative system, with the oxygen transferred by direct contact between the slime and atmosphere as well as air entrainment in the turbulence associated with the rotation. The system overcomes some of the disadvantages of the stationary trickling filter approach which includes the continuous shearing of the fixed biomass as the discs pass through the water thus preventing an accumulation of surface growth, and an effective penetration of oxygen through the outer layers of the biomass. It has lower energy requirements than the activated sludge system, particularly when mixing rather than oxygen controls design. Two other advantages which are proposed but not yet demonstrated in the refining and petrochemical industry is the fact that suspended solids in RBS effluents are lower than those from activated sludge systems and nitrification can be better accomplished by concentrating the nitrifying microorganisms in the latter stages of discs on the shaft, and adjusting the pH in the nitrifying stages to maximize the biochemical oxidation of ammonia. If the organic concentration of the industrial wastewater is high (the BOD_5 exceeds 1,000 mg/l for example) the capital costs and energy requirements of the RBS system over activated sludge may be reduced. Moreover, if many of the organic compounds are refractory and require long contact periods for adequate degradation, the effective biological growth-substrate contact may be insufficient to reduce these refractory compounds to the required level. Therefore, one should be certain that the RBS system can reduce the COD level adequately before making the final process selection.

Process Flexibility for Biological Systems

One of the primary limitations in applying the biological method of treating industrial wastewaters has been the failure to incorporate proper pretreatment and process flexibility facets into the basic design. As the biochemical oxidative mechanisms are complex, particularly for industrial wastewaters discharged from the refining, petrochemical and organic chemical industries, every effort must be made to accommodate the biological population to the maximum extent. Some of the approaches which can be used in insuring process flexibility are discussed in the following paragraph.

Equalization can be one of the most critical single processes in the overall biological treatment facility. The deleterious effect of transient loadings on biological systems, both hydraulic and organic, is well documented (Ref. 2 and 3). There are several rational methods which can be utilized from raw waste load variations in size and equalization basins in order to dampen influent variations (Ref. 4 and 5). It is also prudent to include auxiliary "off-specification" basins in the biological process design in order to temporarily receive and store waters of inordinately high organic concentrations or those with potential toxicity. This water can then be pumped from inventory back to the biological system at a controlled hydraulic rate. Diversion of the wastewater stream can be accomplished automatically using an on-line analyzer. Such basins, along with equalization, reduce the hydraulic and organic variations to the biological systems and normally result in significantly higher overall removal efficiency.

Specific pretreatment steps of industrial waste are often effective in enhancing the overall performance. For example, it may be prudent to dilute the concentration of highly degradable organic constituents to a concentration level which will allow more effective biochemical oxidation of organic compounds. This is true when biochemical inhibition can occur which is attributed strictly to influent organic concentration rather than to constituent complexity or resistance to biodegradation. Predilution in this case is a legitimate and appropriate pretreatment step to improve the overall performance of the biological system, particularly when recognizing that kinetics of removal are more concentration-sensitive than mass-sensitive. Another pretreatment approach which can be considered is the steam or solvent stripping of selected waste streams, with proper air emission control measures as applicable. This approach can reduce high organic loads, sequester organic load variations, and remove potentially toxic or inhibitory contaminants, improving the amenability of the stream to biological treatment. Probably the most common example of this pretreatment is sour water stripping in petroleum refineries, but there are numerous other instances in the chemical processing industry where this is an effective pretreatment step. Recent practice has indicated that hydrolyzing selected organic wastewater streams by adding caustic and exercising pH control can enhance the biodegradability of the hydrolyzed stream (Ref. 6). This practice has been applied as a pretreatment step in the biological treatment of pesticide and herbicide waste streams with positive results.

One operational technique which can provide additional resistance to biological upset is increasing the inventory of biological solids in the aeration basin of a fluidized activated sludge process. This can be accomplished by increasing the sludge recycle ratio and/or reducing sludge wastage. The increased inventory simply implies that the quantity of biotoxic or biostatic constituents per bacteria is reduced. The design MLSS levels in activated sludge systems typically range from 2500 to 3000 mg/l while in some cases for industrial applications, the MLSS level are maintained from 8000 to 10,000 mg/l (Ref. 7).

Process Optimization of Biological Systems

When considering advanced treatment systems, one assumes the biological portion of the facility is designed and operated for maximum performance. This may not be the case and some discussion is therefore merited.

Sludge Age Sludge age, or the average contact time between the microorganism and the substrate, is becoming increasingly popular as a process control parameter (Ref. 6, 7). Sludge age can be defined mathematically using several approaches, the most common for activated sludge being:

$$\Theta_c = \frac{X_a \cdot V}{\Delta X} \qquad (1)$$

where:

Θ_c = sludge age, days
$X_a \cdot V$ = average aeration basin MLVSS, mass (V = basin volume)
ΔX = sludge wastage, mass per day

In a controlled reactor, the sludge age is similarly defined as:

$$\Theta_c = \frac{X_a \cdot V}{Q_w X} + (Q-Q_w)X_e \qquad (2)$$

where:

Q = total system flow
Q_w = solids wastage flow
X = solids wastage concentration
X_e = effluent solids concentration

The sludge age and the more commonly used Food-to-Microorganism (F/M) ratio can be related in the following manner:

$$\frac{1}{\Theta_c} = \frac{a(\Delta F/\Delta T)}{X_a \cdot V} - b \tag{3}$$

where:

a = sludge yield coefficient
$\Delta F/\Delta T$ = the mass (lbs) of food (COD or BOD) per day removed
$X_a \cdot V$ = the mass (lbs) of microorganisms in the aeration basin
b = the endogenous rate coefficient

The hydraulic retention time, t, and its interrelationship to sludge age has not been adequately defined in terms of process kinetics, although such a relationship would be particularly meaningful in developing design equations. There are many indications that contact time between the biomass and the waste constituents, as measured by hydraulic retention time, can also be an important process parameter for treatment of complex organic wastewaters.

Recent investigations have suggested that sludge age is the best control parameter, and, contrary to some theories, an extended sludge age of forty days or more maximizes performance in terms of sludge settleability, process control, and organic removal efficiency (Ref. 8). Other studies have shown that the critical sludge age (defined as the minimum Θ_c necessary to achieve maximum organic removal) is a function of substrate and temperature, but does not exceed six to seven days even for a complex chemical waste at temperatures of less than 10°C (Ref. 9). It can only be concluded from these investigations that the optimum sludge age for an activated sludge system treating industrial wastewaters is dependent on the nature of the influent, namely, its concentration and complexity, and the operating temperature of the aeration basin. In other words, sludge age alone does not adequately define the ability of a suspended-growth biological system to provide maximum removal of organics from a specific wastewater. The Food-to-Microorganism ratio (F/M) and hydraulic retention time are also important control criteria in some cases. Treatability studies are thereby justified to establish the design Θ_c and other control parameters specific to the industrial waste and the most severe operating condition.

Temperature

It is important to pursue the temperature effects on biological systems, as the Streeter-Phelp's empirical modification of Arrhenius' law has not always held in predicting reaction rate coefficients at defined temperatures. This equation is stated as follows:

$$K_T = K_{T_1} \Theta^{(T-T_1)} \tag{4}$$

where:

K_T = the reaction rate at temperature, T

K_{T_1} = the reaction rate at temperature T_1

Θ = the temperature activity coefficient which is a constant for a given wastewater

It has been proposed for several years that colder temperatures in the aeration basins have a more pronounced effect in terms of reduced process efficiency for wastewaters of higher molecular complexity and solubility (Ref. 8). This has recently been confirmed by determining the critical sludge age for wastewaters of varying complexity undergoing aeration at several temperatures as shown in Figures 1, 2, and 3 (Ref. 9). Based on these studies, the critical sludge age for each temperature and wastewater can be approximated as follows:

	Temperature, °C	Critical Sludge Age, Days
Domestic Wastewater	30°	2
	10°	3.5
Chemical Wastewater	30°	2.5
	10°	5.5
Petrochemical Wastewater	30°	3.5
	10°	8

It is of paramount importance, therefore, that designers provide sludge ages which are adequate for maximum performance predicated on wastewater complexity and swings in operating temperatures. This is particularly important for systems with long hydraulic retention times since aeration basin temperatures will approach ambient air temperature even if the wastewater is quite warm before aeration.

Bulking Sludge

The solids-liquid separation phase of biological treatment has always been one of the more important elements in successfully treating wastewater using this system. Bulking sludge is one of the main precursors to high effluent TSS levels and consequently has received much attention in the attempt to optimize biological treatment facilities. Sludge bulking is particularly prominent in the food processing industries, primarily based on the fact that an easily available carbon source tends to promote filamentous microorganisms. However, sludge bulking also occurs in many other industrial categories, and consequently occupies a role of primary importance in evaluating methods of process control. Historically, bulking is extremely difficult to correct once it has occurred and thus, a preventive approach is generally most successful. As filamentous microorganisms tend to thrive at lower pH, oxygen tension, and nutrient levels than do the flocculating microflora, it is important to insure adequate pH control, sufficient aeration, and an adequate supply of nitrogen and phosphorus to the system. The use of dissolved air flotation with polymer addition as the final clarification step is receiving an increasing amount of attention. If the wastewater contains an easily available carbon and filamentous organisms tend to historically persist, dissolved air flotation with chemical addition facilities should be given careful consideration. It must be recognized, however, that effluent TSS concentrations from biological systems using DAF as the first cell separation step will range, as for conventional activated sludge systems, from 25 to 75 mg/l which still may be inadequate to meet criteria, necessitating effluent polishing.

Preliminary results in evaluating contact stabilization against completely mixed activated sludge for treating one industrial waste indicates that the activated sludge system is less prone to produce a filamentous population and thus less susceptible to sludge bulking. This is possibly attributed to the fact that in the contact stabilization approach, a higher food-to-microorganism ratio in the contact tank promotes more filaments which persist through the reaeration phase of the process. For this reason, conversion of contact stabilization to completely mixed activated sludge may enhance overall sludge settleability and process performance in systems with bulking problems.

The addition of chemicals such as hydrogen peroxide to the aeration basin or recycle sludge to minimize sludge bulking has had mixed success, although operating costs are a significant factor if the procedure must be implemented continuously to prevent recurrence of the problem. The concept of biodynamic control using a controlled seeding of sludge microflora to a biological waste system treating food and dairy wastewaters has recently been reported as an effective method of minimizing sludge bulking (Ref. 10). Although this is a theoretically sound concept, the practicality of controlled seeding in large biological systems should be verified in terms of process and cost effectiveness before such an approach is given serious consideration.

Optimization of Biological Nitrification

Stringent effluent ammonia concentration levels required by many permits has necessitated the use of nitrification in many industrial biological treatment systems. As nitrifying microorganisms are extremely sensitive to pH and temperature, and since many process variables and trace chemical constituents affect their performance, it is capricious to predict nitrification strictly on sludge age or hydraulic retention time. Consequently, designers of biological systems are having to use more sophisticated concepts in order to insure the biological removal of ammonia nitrogen from industrial wastes. The concept of two-stage activated sludge has been proposed, utilizing the advantages of isolating the nitrifying microorganisms in a second state while minimizing nitrifying inhibition factors in the first stage of aeration (Ref. 11). Such a concept, although considerably more expensive than a single-stage system, does provide more process control for enhancing nitrification. For example, the nitrifying reduction attributed to winter temperatures can be partially offset by increasing the recycle ratio of the nitrifying-rich sludge in the second stage, enhancing the overall nitrification during the critical seasons of the year.

A recent study indicated that an aerobic submerged filter may be a feasible approach for the economical nitrification of low-strength wastes (Ref. 12). This system provides an upward flow of liquid through plastic or natural media and through efficient solids capture and control of hydraulic detention time, stable nitrification has been reported. Surface area effects on nitrification are not well documented, but undoubtedly are significant when comparing suspended and fixed-growth systems relative to nitrification.

The rotating biological surface (RBS) has also been quite successful in biologically treating ammonia nitrogen. A properly-designed RBS system offers inherently the same advantages as a two-stage activated sludge system, namely, allowing an enriched nitrifying population to develop in the latter stages of the RBS process. As the pH tends to drop through an RBS system via the production of carbon dioxide, it may be necessary to adjust pH in the nitrification stages by the addition of caustic to raise the pH level to the nitrification optimum of 7.5 to 8.3. It is important to recognize that 7.1 of alkalinity (as calcium carbonate) can be destroyed per unit of ammonium ion (as nitrogen) nitrified, underscoring the need for good pH control, particularly for wastewaters with low alkalinity.

It should be noted that there have been several process problems in terms of nitrification when high amine concentrations are present in the wastewater, probably through biochemical cleavage reactions of the amine functional group, actually creating ammonia biochemically in the biological system.

A particular problem in applying nitrification to industrial wastewaters is the sensitivity of the nitrifying bacteria to a wide variety of identified and unidentified organic and inorganic chemicals. This is especially a problem with complex wastewaters such as those of the chemical processing industries. All other conditions being proper, nitrification may still not be obtained for a given wastewater unless the inhibitory components are found and removed. This problem makes it mandatory that bench and/or pilot-scale treatability studies on the actual wastewater to be treated be conducted prior to design of nitrification into a biological treatment system. Often, the treatability studies can identify certain waste streams and/or components which can be removed or pretreated to promote nitrification of the total waste stream.

EFFLUENT POLISHING

Polishing the effluent from biological treatment systems clearly constitutes "advanced waste treatment" and is the model for BPCTCA and/or BATEA levels of technology for several industrial categories. As previously mentioned, there are several approaches for improving biologically treated effluent quality. The methods discussed here include chemical addition, powdered activated carbon addition to activated sludge systems, post filtration, and fixed-bed carbon polishing units.

Chemical Addition

The addition of coagulants or coagulant aids between the aeration basin and the final clarifier often can enhance quality by reducing TSS and colloidal materials in the final effluent. The organic oxygen demanding substances associated with these suspended and colloidal materials are correspondingly removed.

There have been mixed results as to the efficacy of this approach. Normally, polymer additions in the range of 1 to 5 mg/l result in a 10 to 20 percent reduction in effluent TSS from an activated sludge system, although this may vary. One of the more favorable experiences of adding polyelectrolytes to an activated sludge system treating petroleum refinery wastewaters is shown in Figure 4. As shown in this case, better than fifty percent of the TSS were removed upon the additon of approximately 5 mg/l of the polyelectrolyte. There are many variables which influence the applicability of adding coagulants or coagulant aids to enhance the clarification of biologically treated effluents, however, so test conformation studies should be performed. Moreover, polyelectrolytes are very expensive and high concentration demands would result in excessive operating costs. The installation of a chemical feed system and mixing basin also would require a capital expenditure.

Powdered Activated Carbon Treatment

The addition of powdered activated carbon to activated sludge systems to enhance settleability and remove residual organic materials has been proposed for several years and has been implemented on several occasions. The addition of 450 mg/l of powdered activated carbon to an activated sludge aeration basin treating refinery wastewaters resulted in a relatively substantial increase in process performance as shown in Figures 5 and 6 (Ref. 13). This approach was not considered as a long-term corrective measure, however, based on the difficulties in handling the powdered carbon around the aeration basin.

The most significant project currently in operation which utilizes powdered activated carbon and a biological mass and aeration system is the 40 MGD DuPont-Chambers Works Facility. The initial results indicate good performance in terms of effluent quality, although the efficacy of dewatering, incineration, and regeneration of the mixed biological-carbon sludge has not been proven and could represent the critical path in the overall applicability of this approach (Ref. 14). Required carbon dosages and the ability to reuse the adsorbent material obviously will dictate the cost-effectiveness of this approach as compared to other alternatives.

As with the chemical addition option described above, only actual testing of the method and careful cost analyses can determine its applicability to a particular wastewater. Both bench and pilot treatability studies as well as the experimental use of powdered carbon in the full-scale system, if possible, should be used in the evaluation process.

Post Filtration

Post filtration of biologically treated effluents has been applied in several industrial wastewater treatment facilities, and in fact, used as the BPCTCA model for developing the petroleum refining guidelines. Post filtration systems, based on field performance, do a reasonably good job of reducing the effluent TSS concentration to 10 to 15 mg/l, although chemical addition to the filter influent is often required to strengthen the floc and make it more filterable. Additionally, there is a practical limit of 80 to 110 mg/l of TSS which can be charged to the filter, an excess of which causes inordinately short run times and reduces the practicality of the filter process.

The operating biological treatment-post filtration systems treating refinery and petrochemical wastewaters are producing effluents with long-term TSS averages of 10-15 mg/l. The efficiency of a post filtration system depends to some degree on the influent TSS concentration as shown in Figures 7 and 8. The data presented in Figure 7 was developed from studies using pilot-scale filters receiving a biologically treated effluent. It is noted that the addition of polymers to both the deep bed and shallow bed downflow filters made the overall filter performance less dependent on influent TSS, an inherent advantage of the polymer addition. The data in Figure 8 were developed in pilot-scale downflow filtration studies, indicating the same trend and TSS residual concentrations. The reduction of oil and grease (O&G) compounds attributed to the addition of post-filters is not dramatic, as indicated in Figures 9 and 10 (Ref. 15). The probability distribution of O&G in biologically treated effluent from case histories in the petroleum refining industry indicate a range of 3 to 15 mg/l (median values) as shown in Figure 9 while the two systems in the refining industry which have filters shown in Figure 10 produce a median value O&G concentration of 7 to 8 mg/l.

Activated Carbon Polishing

There are presently no full-scale operating biological fixed-bed carbon polishing treatment facilities treating refinery, petrochemical, or organic chemical wastewaters for which data are available, although some are reportedly close to beginning operations. For this reason, pilot-scale studies must be used as the data base. The COD removal in carbon columns polishing activated sludge effluent as determined in various pilot-plant studies for petrochemical and refinery plants is tabulated in Table 1 (Ref. 16). A 59 to 83 percent removal is noted, indicating that residual COD can be further reduced in such an application. This is true because there is an inherent process compatibility between biological and carbon treatment as many compounds resistant to biochemical degradation are amenable to carbon adsorption (Ref. 17). It should be recognized, however, that the cost-effectiveness of carbon polishing expressed in lbs of BOD or COD removed per cost unit is poor, based on the high cost of removing a relatively low mass of residual compounds. For this reason, every effort should be made to select less costly modes of effluent polishing if regulatory constraints so allow.

Activated carbon, applied as a process in a physical-chemical system treating these industrial wastewaters is less applicable, as discussed in the following section.

PHYSICAL-CHEMICAL SYSTEMS

Most of the previous studies relative to the physical-chemical treatment of industrial wastewaters has centered around activated carbon treatment, although steam and solvent stripping, chemical oxidation, chemical coagulation and precipitation, and other forms of non-biological treatment are possibly applicable.

It should first be understood that activated carbon treatment of organic industrial wastewaters should be carefully investigated prior to making process commitments. Several studies, for example, have underscored the limitations of activated carbon as total physical-chemical treatment process as compared to carbon polishing of biologically treated effluent (Ref. 16, 17, 18, 19). The estimated effluent quality for the activated sludge, carbon, and combined treatment of refinery wastewaters are tabulated in Table 2 (Ref. 18). A more recent study comparing activated carbon as a physical-chemical or polishing process was conducted by the Environmental Protection Agency (Ref. 20). Both API Separator effluent and biologically-treated effluent from a petroleum refinery were charged to pilot-scale columns in order to obtain a comparative evaluation. These quality data indicated that the carbon system was significantly more effective when operated in conjunction with the biological process than when applied singularly, both in terms of BOD and COD. This is consistent with the results observed in pilot studies conducted by the author. The limitations of physical-chemical systems designed around the activated carbon adsorption process therefore are a function of the organic compounds in the wastewater which are not amenable to adsorption, reducing overall efficiency. Even though physical-chemical systems have more of an "advanced waste treatment" connotation, they could, in fact, produce a lower effluent quality than biological treatment processes.

SUMMARY

In summary, it is the author's opinion that "advanced waste treatment" for the petroleum refinery and organic chemical industries centers around some form of biological treatment, at least for the next decade. There are no direct alternatives which are presently as cost-effective in terms of chemicals or energy, and there are few likely process candidates which are likely to be more attractive, at least through the 1983 date for implementation of Best Available Treatment Economically Achievable. Physical-chemical treatment is and will continue to serve as an important adjunct, primarily as pretreatment of specialty streams or as polishing units in series with biological processes. Although sole physical-chemical processes are possibly applicable in certain cases, careful conceptual planning and process confirmation through treatability studies should precede final selection.

The applicability of the activated carbon process in treating industrial wastewaters, for example, is contingent on many factors, including the amenability of the dissolved constituents to sorption, the presence of other substances which enhance or impede the sorption process, the soundness of engineering, the degree of pretreatment and proper operation and maintenance of the system. As activated carbon was one of the primary processes factored into the development of the 1983 Best Available Technology (BAT) guidelines for many industrial categories, some of which have been remanded by the Courts, it is important to fully understand the process and its limitations.

Finally, it is important to recognize that "advanced waste treatment" in effect will have an EPA definition when the BPT, BAT, and new source performance standards for the Organic Chemicals and Plastics and Synthetics categories, and the BAT standards for the Petroleum Refining category are repromulgated later this year.

DISCUSSION

Garr M. Jones, Brown and Caldwell: We have noticed that in many industries and their municipal wastewater treatment systems the advantages of what we call a coupled system, a fixed-growth system followed immediately by activated sludge. I noticed that you passed over this particular combination and I would like to ask you to comment on the advantages that we see, first of all lower operating costs, smaller clarifiers because of improved solid settling of characteristics, and a far more stable process.

Davis Ford: Yes, I would say that would have the same basic process concept as the trickling filters did in the past, and I think from the process point of view it makes a lot of sense. You say there are lower operating costs; I would only caution there that if you take the capital cost of that system and amortize that and include the operating costs and it still is cheaper, then that certainly can be justified on an economical basis. From the process point of view I would say the addition of a fixed-growth reactor before or even after activated sludge has some merit certainly to be investigated. I certainly agree with that concept.

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TABLE 1

CARBON PILOT-PLANT RESULTS FOR POLISHING PETROCHEMICAL AND REFINING WASTEWATERS (REF. 17)

Type of Wastewater	Design Q (MGD)	Influent COD (mg/l)	Effluent COD (mg/l)	Percent Removal
Petrochemical	3	150	49	67
Refinery	26	100	41	59
Refinery	28	300	50	83
Refinery	8	100	40	60
Petrochemical	29	150	48	68

Table 2

Estimated Effluent Quality for the Activated Sludge, Carbon, and Combined Treatment of Refinery Wastewaters*(Ref. 19)

Constituent	Mean Value Range Primary Effluent	Activated Sludge Effluent	Total Carbon Effluent	Combined Activated Sludge-Carbon Effluent	Remarks
COD	500-700 mg/1	100-200 mg/1	100-200 mg/1	30-100 mg/1	Exact COD residuals vary with complexity of refinery & design contact times in the Act.S. and Carbon Treatment Plants.
BOD_5	250-350 mg/1	20-50 mg/1	40-100 mg/1	5-30 mg/1	BOD residual depends on BOD/COD ratio which characterizes relative biodegradability of wastewater.
Phenols	10-100 mg/1	<1 mg/1	<1 mg/1	<1 mg/1	Phenols(ics) are generally amenable to biological and sorption removal.
pH	8.5-9.5	7-8.5	7-8.5	7-8.5	pH drop in Act. S. systems attributed to biological production of CO_2 and intermediate acids. pH change in carbon columns depends on preferential adsorption of acidic and basic organics.
SS	50-200 mg/1	20-50 mg/1	<20 mg/1	<20 mg/1	Primary effluent solids depend on design and operation of oil removal units. Act. S. effluent solids depend on effectiveness of secondary clarified. Low effluent solids characterize carbon column effluent.
TDS	1500-3000 mg/1	1500-3000 mg/1	1500-3000 mg/1	1500-3000 mg/1	TDS is essentially unchanged through all three treatment systems.
NH_3-N	15-150 mg/1	1-30 mg/1	10-140 mg/1	1-30 mg/1	Exact concentration depends on prestripping facilities, nitrogen content of crudge charge, corrosion additive practice and biological nitrification.
P	1-10 mg/1	<1-7 mg/1	1-10 mg/1	<1-7 mg/1	Only removal attributed to biological synthesis.

*Based on wastewater characterization data and treatability studies conducted by the author at eight refineries and petrochemical installations.

FIGURE 1 EFFECTS OF SLUDGE AGE AND TEMPERATURE ON BIODEGRADABILITY (REF. 9)

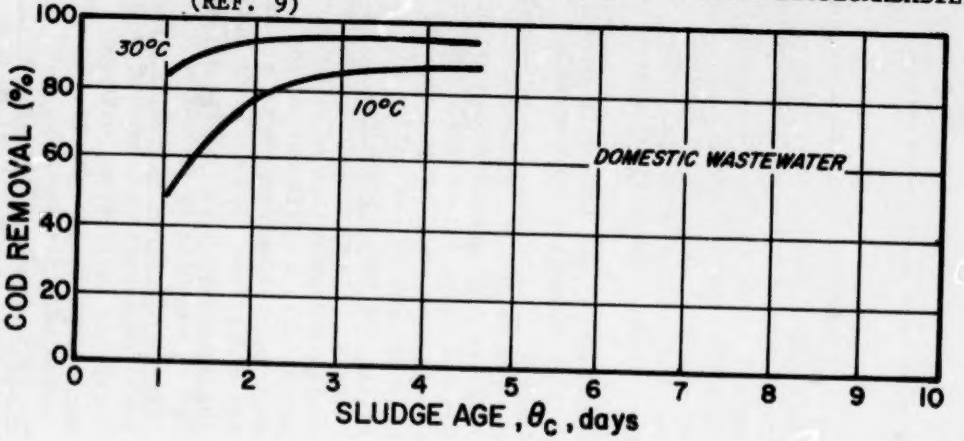


FIGURE 2 EFFECTS OF SLUDGE AGE AND TEMPERATURE ON BIODEGRADABILITY (REF. 9)

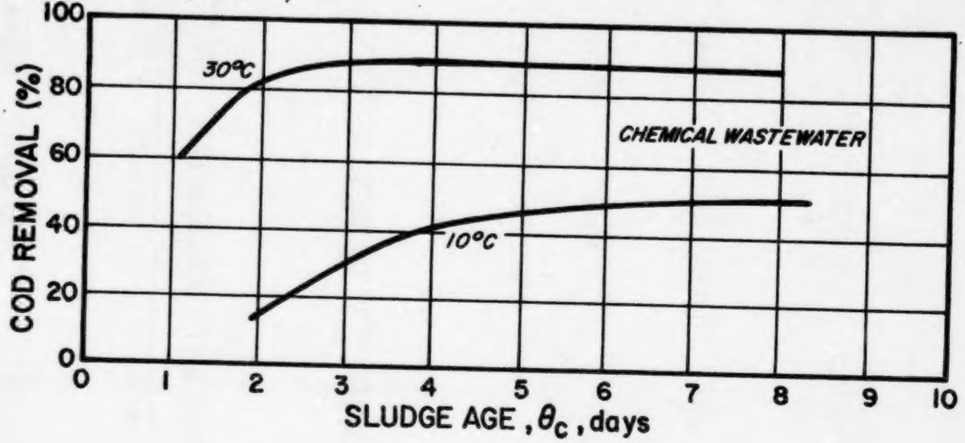


FIGURE 3 EFFECTS OF SLUDGE AGE AND TEMPERATURE ON BIODEGRADABILITY (REF. 9)

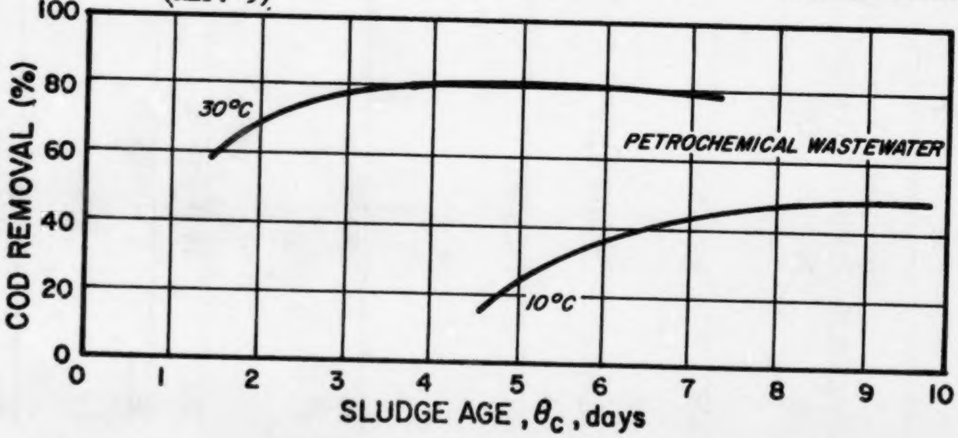


FIGURE 4

EFFECT OF POLYELECTROLYTE ADDITION
ON EFFLUENT TSS
FLOW PROBABILITY DISTRIBUTION

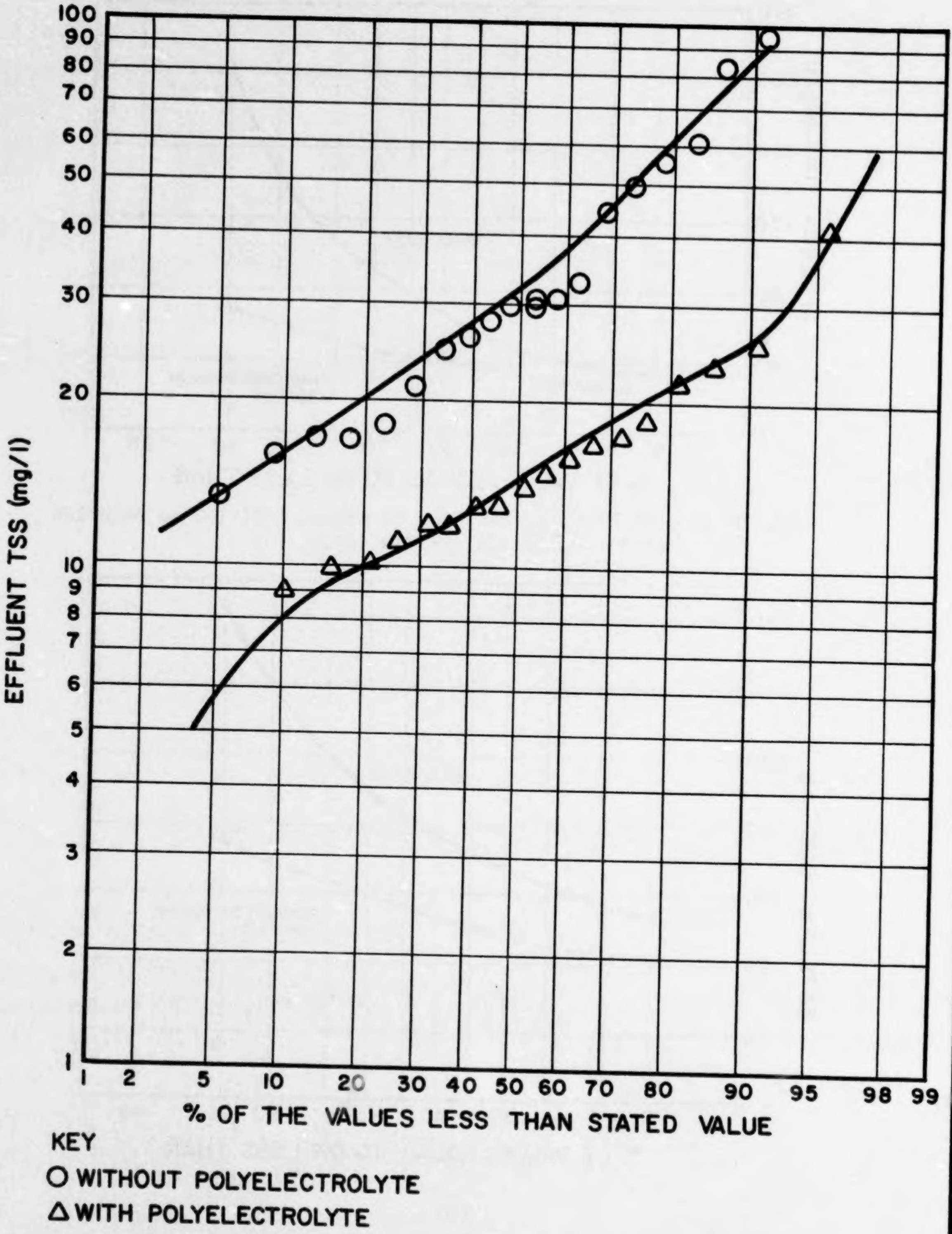


FIGURE 5 EFFECT OF EFFLUENT TSS OF CARBON ADDITION TO AERATION BASIN - PETROLEUM REFINERY (REF. 13)

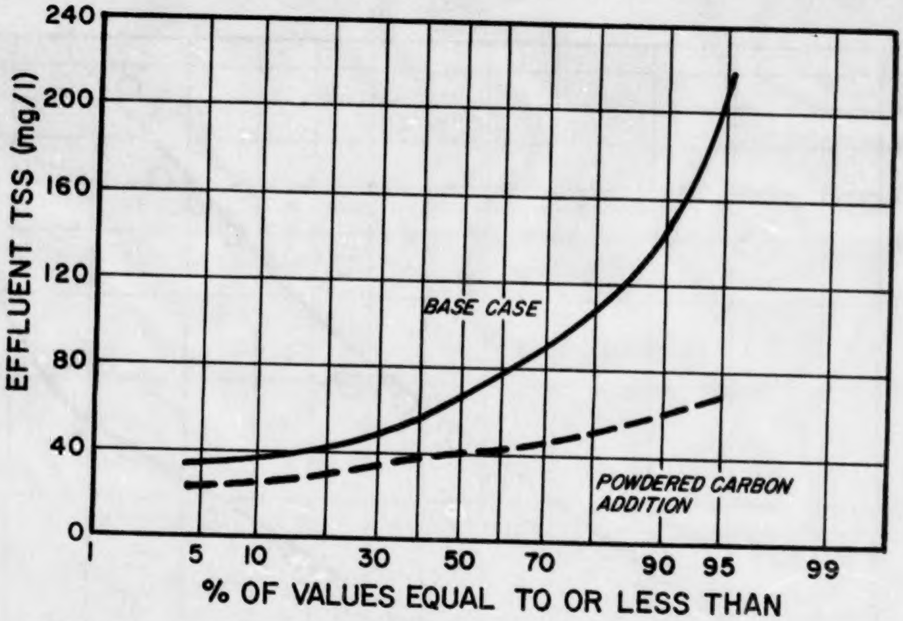


FIGURE 6 EFFECT OF EFFLUENT COD OF CARBON ADDITION TO AERATION BASIN - PETROLEUM REFINERY (REF. 13)

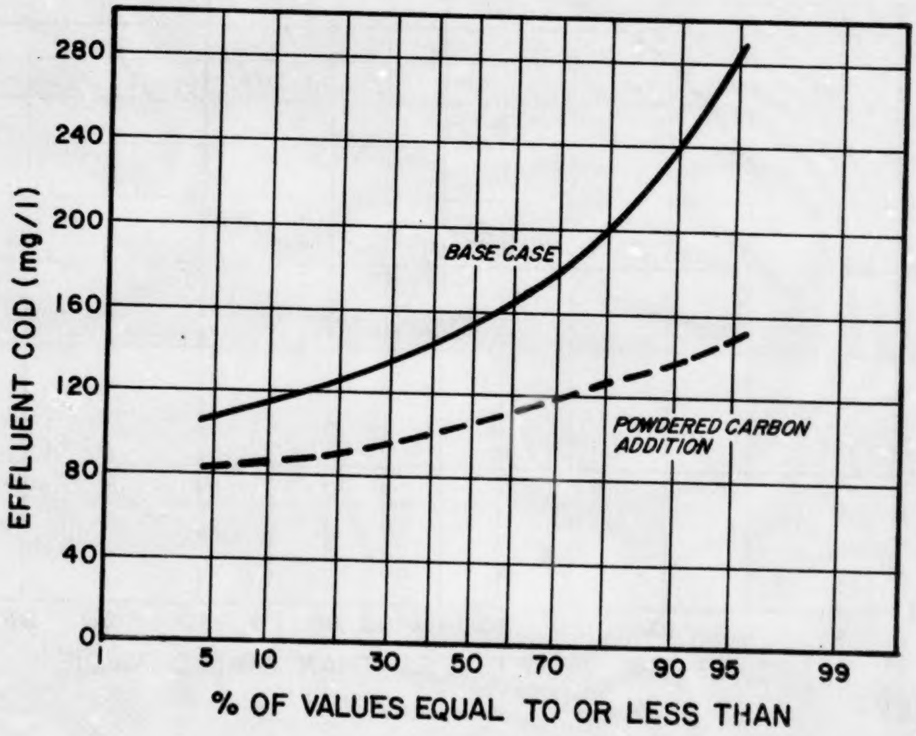


Figure 7

POST FILTRATION PERFORMANCE– PILOT SCALE DEEP BED AND SHALLOW BED DOWNFLOW FILTERS WITH AND WITHOUT POLYMER ADDITION

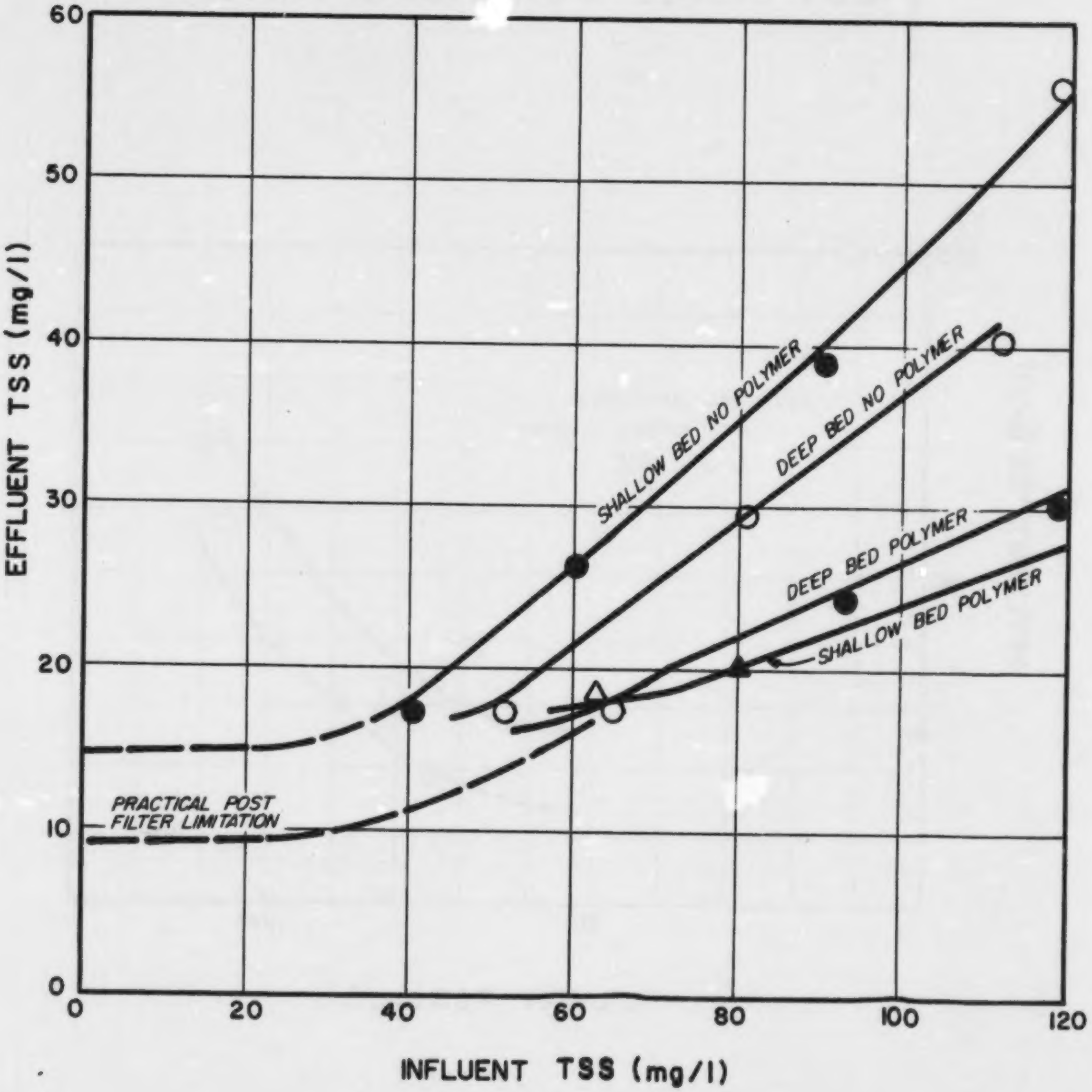


Figure 8

POST FILTRATION PERFORMANCE–PILOT SCALE DOWNFLOW FILTERS

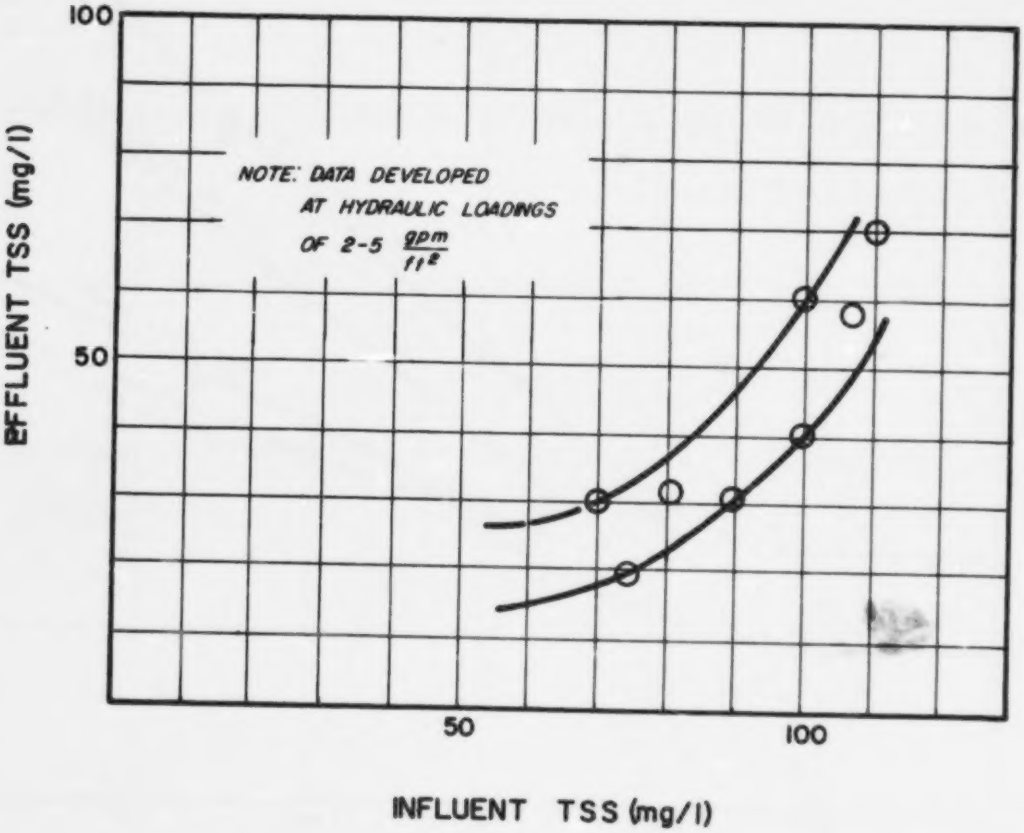


Figure 9

OIL AND GREASE PROBABILITY BIOLOGICAL TREATMENT

(REF. 15)

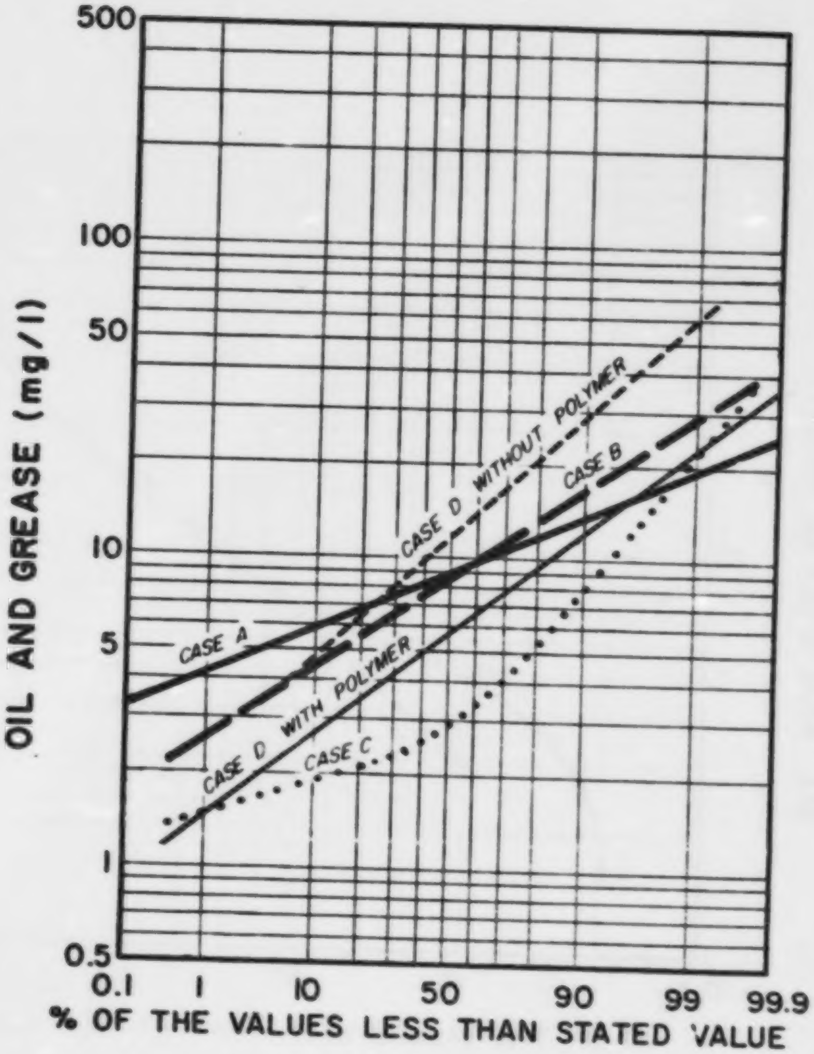
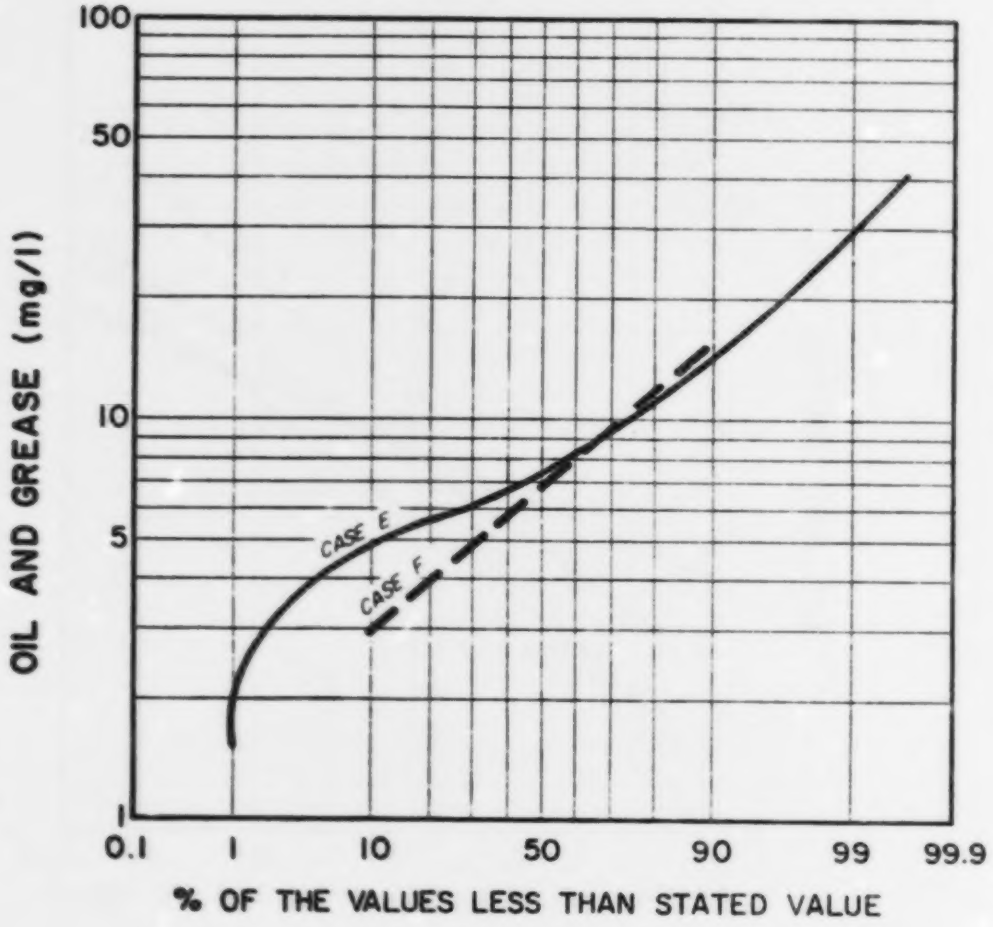


Figure 10

OIL AND GREASE PROBABILITY BIOLOGICAL TREATMENT WITH POST-FILTRATION

(REF. 15)



SESSION VI

FUTURE CONSIDERATIONS IN BIOTREATMENT

Chairman

George W. Reid

Regents Professor of Civil Engineering
University of Oklahoma, Norman, Oklahoma

Speakers

J. F. Grutsch

R. C. Mallatt

"Design and Operation: Bases for an Activated Sludge Route to BAT (1983) Water Quality Goals"

Paul Goldstein and Robert W. Griffin
"Considerations in Reuse of Refinery Wastewater"

Milton R. Beychok
"State-of-the-Art in Sour Water Stripping"

Irv Kornfeld and Jay G. Kremer
"Refinery Discharges to a Large Municipal Sewerage System"

BIOGRAPHY George W. Reid

George W. Reid, born 1917, Indianapolis, Indiana, attended Shortridge High School, Purdue, Harvard and Johns Hopkins Universities, studying Civil and Sanitary Engineering. Employed by the Indiana State Health Department, a sanitary engineer with USPHS, MCWA and CDC. Has taught at Purdue, Johns Hopkins, Florida and George Tech. Currently teaching at the University of Oklahoma as Regents Professor of Civil Engineering and Environmental Sciences and is the Director of the Bureau of Water and Environmental Resources Research. Holds degrees from Purdue and Harvard Universities.

Has published numerous articles, etc., in the field (170); is and has been consultant to the USPHS, EPA, Interior, USAF, WHO (PAHO), AID and others in water and public resources systems. Recently involved in extensive research on modeling of natural and man-made public systems. Lectures at recent Urban Water Systems Conferences and seminars in Colorado, New Mexico, Bogota, Lima, Europe, etc.

DESIGN AND OPERATION: BASES FOR AN ACTIVATED SLUDGE ROUTE TO BAT (1983) WATER QUALITY GOALS

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ABSTRACT

Since its debut 65 years ago, the activated sludge process (ASP) has been developed into a widely applicable process with a tremendous capacity for water purification. Unfortunately, the role of the ASP has become essentially totally identified with secondary treatment, that is, best practicable control technology currently available (BPT) goals for 1977. When effluent water quality superior to that normally associated with BPT levels is a goal, for example, best available technology economically achievable (BAT), an add-on stage of granular carbon treatment is the typical response for organics reductions.

Current work is demonstrating that viewing the ASP solely as a secondary treatment process is shortsighted and, in fact, the ASP provides the preferred means for achieving BAT water quality goals when compared to alternatives. A cost effective route for using the ASP to achieve BAT effluent quality requires that the ASP be operated at unusually high sludge age and enhanced with high surface-area activated carbon.

Other reports at this Second Open Forum will describe the successful enhancement of the ASP using powdered activated carbon; this paper, therefore, will focus on describing: 1) How ASP operation at very high sludge age is achieved; 2) The support biological and kinetic data give to defining, as being optimal, the ASP operating conditions required to operate at very high sludge age, and 3) ASP process-design optimization at very high sludge age.

INTRODUCTION

At the May, 1977, API meeting, two papers (1,2) presented an alternative to granular carbon adsorption treatment of activated sludge unit (ASU) effluent to achieve "best available technology economically achievable" (BAT) proposed for 1983. The alternate approach to BAT incorporates the use of newly developed, ultra-high surface-area powdered active carbon (PAC) in the ASU of the "best practicable control technology currently available" (BPT) model sequence for 1977. The alternate eliminates essentially all the capital costs of the granular carbon system. Further, operating costs for PAC can be minimized by optimizing operation of the end-of-pipe sequence.

Optimization of the end-of-pipe sequence for the PAC alternate to granular carbon treatment requires that the role of the ASU and other end-of-pipe treatment elements be defined as we described at the First Open Forum (3). A summary of the operating guidelines follows:

1. A systems optimization of a refinery end-of-pipe treatment sequence points to the ASU as the key element.
2. To achieve maximum water quality, system optimization points to reversing the historic work-horse role of the ASU; i.e., it should be used only for the removal of essentially soluble contaminants.
3. Reversing the role of the ASU yields a dramatic series of beneficial effects. At very high sludge age:
    a. The SVI characteristics of the activated sludge mass are excellent.
    b. Process control is greatly simplified.
    c. The need for many process control tests is eliminated.
    d. An exemplary effluent low in TOC and other contaminants is produced.
    e. The net cell yield is remarkably low.
    f. The population dynamics of the sludge mass improve.
    g. Maximum ASU capacity for purification is achieved.
4. Systems optimization, wherein the key element is using the ASU for removal of only soluble contaminants, permits clear definition of the roles the other elements play; i.e., colloidal and suspended matter must be essentially all removed in pretreatment sections.
5. The technology is available to handle the new requirements made by the process operations in their changed roles.
6. Current research developments on cell membranes and enzyme systems support strongly this new role for the ASU.
7. Cell genetics, wherein inducible enzymes or mutant species are required, support operating the ASU at very high sludge age for maximum purification capacity.
8. Bacteria are essentially enzyme factories. Enzymes are sensitive to temperature, pH, excessive concentrations of heavy metals, oxidizing agents, salinity, UV, and other radiations.

Using the ASU for removal of only soluble contaminants is consistent with obtaining a stable system less influenced by transient changes in environmental conditions since the endoenzyme systems are at least partially protected from these environmental changes by the bacterial cell wall and membrane.

9. This recommended systems optimization saves significant energy and other operating and capital costs of the end-of-pipe sequence.

10. This recommended systems optimization minimizes the generation of solid wastes, and the solid wastes generated are amenable to disposition.

The objectives of this paper are:

1. Outline how an ASU can be operated at high sludge age (50+ days) by outlining and describing in detail the chemistry of colloid destabilization which must be addressed if the pretreatment (filter and dissolved air flotation) are to remove colloidal solids essentially completely.

2. Propose a model for chemical destabilization of negative colloids by weakly anionic polyelectrolytes.

3. Describe how the electrical properties of the activated sludge floc impact on the mechanical design of the unit.

KINETIC AND BIOLOGICAL DATA SUPPORTING ASU OPERATIONS ON SOLUBLE CONTAMINANTS AT HIGH SLUDGE AGE

Wastes Properties

An intrinsic property of solids in the presence of water is an electrical surface charge. When colloids are being considered, the electrical charge is called zeta potential (ZP). Almost all matter dispersed in spent process water such as oil particles, silt, biocolloids, inorganic colloids, etc., has a negative ZP. This repulsive coulombic charge causes many particles to resist aggregation and settling in primary clarification facilities. In the case of refineries, the chemical oxygen demand (COD) of the contaminants in the effluent from API separators average about 50 per cent soluble and 50 per cent suspended matter (Figure 1).

By comparison, the soluble COD in the effluent from a municipal primary clarifier is substantially less, being about 15-30 per cent (Figure 2). Thus, the colloids and suspended matter represent the major COD component entering secondary treatment.

ASU Kinetic Effects Achieved by the Removal of Colloids and Suspended Solids from the Feed Stream

Provides a Response to Biological Oxidation Kinetics. A recent kinetic equation (equation 1) by Adams, Eckenfelder, and Hovious (4, 5) applicable to a completely mixed ASU predicts that best effluent quality (lowest S_e) will be achieved with the lowest feed strength (S_i):

$$S_e = S_i (S_i - S_e)/KMt \qquad \text{Equation 1}$$

Where, S_e = Soluble organics in effluent (mg/l)
S_i = organics in influent (mg/l)
K = kinetic constant
M = biomass (mg/l)
t = time

The authors points out that $S_i/Mt = F/M$, and letting $F = S_i/Mt$, equation 1 becomes:

$$S_e = S_i/(KF^{-1} + 1) \qquad \text{Equation 2}$$

Equation 2 clearly points out that a low F/M ratio (high sludge age) and low feed strength are associated with optimized ASU operations. Removing colloids and solids in pretreatment facilities has been demonstrated to be an effective means to achieve dramatically better ASU effluent quality (1, 2, 3).

Reasons for improved effluent quality with reduced feed strength can be visualized better with reference to Figure 3. Transport of substrates through the cell membrane counter to concentration gradients is achieved by enzyme transport systems (permeases). Once inside the cell, the substrate molecules are acted upon by a coordinated and sequential series of enzymes; there are several thousand endoenzymes in a single bacterium (6). A small part of the enzyme sequence may be as pictorialized in Figure 4.

Enzymic reactions are reversible. Accumulation of products affects action of any enzyme in either direction as would be expected in chemical equilibria. Under any set of constant conditions, the equilibrium point for an enzyme-catalyzed reaction is constant. There is a constant relationship between concentration of enzyme and concentration of substrate. Up to the point of "saturation" the rate of reaction increases with increase of ratio of one component to the other. With a constant amount of enzyme, increase of substrate increases the rate of reaction until every molecule of enzyme is fully saturated with substrate. Further additions of substrate cannot increase the rate of reaction. Conversely, with a fixed amount of substrate, the rate of reaction increases with the additions of enzyme until all molecules of substrate are in contact with enzyme. Further additions of enzyme do not affect the rate of reaction. In many instances, enzyme-catalyzed reactions appear to proceed in only one direction because the equilibrium point is very far in that direction. In other cases, one or more of the end products may be removed constantly by some mechanism so that the equilibrium is never reached. Under normal conditions in the living cell, enzyme reactions are constantly pushed in this manner toward one or the other side of the reactions. Theoretically, reversible reactions cannot actually reverse when large differences in energy levels are involved since resynthesis cannot be brought about by the same enzymes because they cannot restore the lost energy. To reverse the reaction requires that work be done by other systems of enzymes that capture new energy from other sources (7, 8).

Endoenzymes do not act individually but as parts of coordinated and sequentially operating systems. Whatever effects one portion of the intracellular enzyme system has some effect on all parts. The activity of an enzyme is inhibited by accumulation of the end products of the enzyme-catalyzed reaction. In a sequentially operating enzyme system, excessive accumulation of a reaction product may inhibit the reaction not only of the enzyme manufacturing the reaction product but all prior enzymes in that sequence. This is an important form of automatic control called feedback inhibition. Thus, if a component of the waste substrate periodically is the same as biological intermediate S_{14}, the internal concentration of S_{14} increases which increases the concentration of the preceding intermediates causing more S_{13}, and S_6 to be transported externally, and less S_o to be transported internally; i.e., high residual organics are observed in the solvent phase.

In the presence of excessive amounts of end products, not only is enzyme activity inhibited, but the actual synthesis of the enzymes, themselves, may be repressed. If a cell normally synthesizing a certain substance is supplied with that substance from an extraneous source, not only is activity of the enzyme inhibited, but synthesis of some or all of the enzymes in the production sequence for that substance is repressed until the enzymes are needed again. The result is, of course, higher residual organics in the solvent phase. This is called feedback repression. Differentiation is made between inhibition of the action of the enzymes by their end products (feedback inhibition) and repression of the synthesis of the enzymes themselves by accumulation of end products (feedback repression) in the enzyme sequence (Figure 4). In a sequentially operating system, the end product of each enzyme can be the inducer of the next enzyme in the series and the inhibitor or repressor of the preceding enzyme, thus carrying forward the work of the enzyme factory (9).

If the principle component of the substrate being treated is S_o, various biological intermediates (identified as S_6, S_{13}, S_{14}, and S_{22}) may also have a propensity to be transported externally by the enzyme transport system. Further, if the biological intermediate is three carbon atoms or less, it can diffuse across the cell membrane. Thus, with increasing concentration of S_o for fixed biomass, the concentration of internal biological intermediates will increase. Since enzyme equilibria are similar to chemical equilibria, increasing the concentration of internal biological intermediates (i.e., S_6, S_{13}, S_{14}, and S_{22}) causes their transport outside the membrane as a response and the concentration of external organics increases. Starved systems (high sludge age, low F/M) are predicted from biochemical principles to be lowest in residual soluble substrates.

On the other hand, a complex substrate, S_o, could result in unexpectedly high residual soluble substrates by intermittently supplying a biological intermediate of a more complex substrate which shuts down the degradation of the complex substrate by feedback inhibition or repression.

Permits Operation at High Sludge Age. Minimizing the feed strength by removing colloids and suspended matter not only yields a purer effluent but provides the means to respond to sludge age. Outlined in the schematic of Figure 5 are properties of the BOD/COD materials. The nonorganic and slowly bioxed materials increasingly accumulate in the sludge mass with increasing sludge age causing deterioration of the sludge settling properties (3). This deterioration of sludge settling properties is apparently caused by changing the electrical properties (zeta potential) of the sludge which is discussed in a later section. ASUs can be operated easily at a very high sludge age (50+ days) if the process is protected from colloids which are inert or only extremely slowly biodegraded. Successful operation at high sludge age responds to those soluble components requiring acclimation of the biomass or having a slow biox rate.

The improvement in ASU effluent quality with increasing sludge age typically is uniformly demonstrable up to about 20 days sludge age; for operation higher than 20 days sludge age, improved effluent quality may or may not be observed. This appears to be related to operating temperature and the nature of the substrates. For example, with reference to Figure 6, Curve A is typical of the ease with which organics in municipal and many industrial effluents are removed biologically. ASU operation at low SA is very effective, increasing operation to 20 days SA yields modest effluent-quality improvement and beyond 20 days, no improvement is observable.

At the opposite end of the spectrum are organics that yield a removal curve like E; i.e., similar to nitrification in a refinery effluent. This curve indicates that microorganisms needed for such slow reproducers that high sludge age operation is needed to accumulate sufficient appropriate organisms for organics removal.

Curve B typifies an organic originally removed at a high rate but which generates a biological intermediate that is removed at a much slower rate. The biological intermediate is rate limiting and increasing sludge age is more effective for decreasing organics in the effluent for this example than for an organic typified by curve A.

Curve D is illustrative of organics whose rate limiting reaction is probably the initial, or an early, enzyme reation in the degration sequence and increasing sludge age increases the removal by increasing the enzyme concentration.

Curve C is probably representative of a sequential enzymic reaction series wherein a series of rate limiting reactions are encountered. Thus, increasing sludge age has the effect of increasing the supply of enzymes needed for the reactions in the later stages which measures as reduced organics in the effluent.

As operating temperatures decrease, biological oxidation rates decrease and more microorganisms are needed to achieve the same substrate removal. Thus, the lower the operating temperature, the more pronounced the impact of increasing sludge age. In an Amoco study (1) with parallel units operating at a median temperature of 14°C (57°F) compared to a control unit at 20 days sludge age, the percentage improvement in effluent quality by prefiltration and increasing sludge age from 20 to 60 days is:

	Per Cent Improvement in Effluent Quality By Prefiltration and Increased Sludge Age	
Parameter	Prefiltration	Prefiltration and Increased Sludge Age
SOC	9.4	20.3
SCOD	20	36.3
NH_3-N	-	58.7
Phenolics	-	29.6

On the other hand, when operating at 85°F, Crame (2) reported similar residual organics at sludge ages beyond 20 days.

Minimizes Waste Sludge. Minimizing the feed strength by removing colloids and suspended matter not only yields a purer effluent but provides the means to achieve operation at very high sludge age which provides for minimum waste biosludge production. Bacteria in the activated sludge mass use the energy available in the substrate for two general purposes. As shown in Figure 3, the substrates can be used for 1) cell maintenance energy and 2) the repair and generation of new cell material. The cell maintenance energy requirement gets first call on the substrate resources. If there is substrate left over, the biological system proceeds to increase in response to the available food supply. Thus, to minimize production of waste sludge, it is obvious that the ASU should have a large mass of activated sludge relative to the food supply; i.e., a high sludge age (SA) which is, of course, the same as a low F/M.

The relationship between SA, F/M, maintenance energy, and cell generation has been known for some time (10):

$$\frac{1}{SA} = \frac{a\,(dF/dt)}{M} - b \qquad \text{Equation 3}$$

where, SA = sludge age (days)
a = cell yield coefficient
b = cell maintenance energy coefficient
M = biomass, lbs.
F = COD, lbs.
t = Time

Using this relationship and data from Crame (2) and Grieves et al (1) which are optimized, completely mixed ASUs operating on the soluble substrate in refinery effluents, the following values were calculated for the coefficients a and b at two different temperatures:

	Temp. (F)	a	b
Refinery A	57	.317	.015
Refinery B	85	.3	.03

Comparison with literature data for various wastes suggest these are appropriate coefficient values.

These coefficients and equation 3 can be used to estimate the equilibrium biomass inventory and the resultant waste sludge generation as a function of sludge age as shown in Figure 7. Considering the curves for refinery B to be most typical operating conditions, it is difficult to rationalize the prevailing practice of operating ASUs at 5-15 days SA, a condition generating maximum waste biomass with its attendant high disposal cost. The waste sludge can be reduced by 2/3 by operation at very high SA. The time span to 150 days SA is included because Amoco is operating a test unit at this condition.

Simplifies Process Control. The sludge age method of process control has many advantages which are discussed in detail by Walker (11). Operating at a very high sludge age is even simpler. For example, at 50 days sludge age, 2 per cent of the inventory-activated sludge is wasted. This is such a small amount that sludge wasting can be done on about a twice/week basis.

ASU Biological Effects Achieved by the Removal of Colloids and Suspended Solids from the Feed Stream

Improves Flocculating Capacity of the Activated Sludge. As shown in Figure 8, activated sludge has a bimodal floc size distribution. A good flocculating and settling sludge has a preponderance of large floc mass compared to the fine particle fraction. The large floc mass is, in essence, a biopolymer analogous to a weakly anionic polyelectrolyte-type polymer. Thus, the large floc mass is a biopolymer flocculant, and the fine particles represent the phase to be flocculated. Qualitatively, when the ratio of the two phases overwhelmingly favors the biopolymer as illustrated by the solid line, a good flocculating sludge results. When the fine particles predominate as illustrated by the dotted line, their surface area overwhelms the capacity of the biopolymer for flocculation, and "arms and legs" (turbidity) is observed in the supernatant.

Inert and slowly biologically-oxidized colloids and suspended matter contribute to increasing the amount of fine particles in the sludge mass. Increasing SA increases their accumulation, thereby contributing to the deterioration in sludge flocculating properties. Removing colloids and suspended matter before ASU treatment results in an excellent activated sludge at very high sludge age.

Improves Zeta Potential Probability Distribution of Activated Sludge Particles. Another way of looking at the settling properties of activated sludge and the impact of the fine particle fraction on the settling properties that is much more enlightening in terms of understanding why solids are lost over an ASU final clarifier weir is to examine the zeta potential probability distribution of the activated sludge particles.

Zeta potentials are typically reported as averages which is misleading, always, and particularly in the case of activated sludge. For example, the probability distribution curves in Figure 9 show the median ZP values of a good settling sludge to be -11 mV and a poor settling sludge to be -12 mV. This difference is not only difficult to measure but is really insignificant. What is significant is the slope of the distribution curve and the ZP of the highest-charged particles. If, for example, a ZP of -14 mV or more negative provides enough repulsive force that the fine particles will not flocculate, fully 8 per cent of the solids in the poor settling sludge mass resist flocculation and settling. On the other hand, essentially all the particles in the good settling sludge are well below -14 mV ZP and flocculate well. Limiting the accumulation of colloids in the activated sludge by effective phase removal in pretreatment facilities is a principal means to control the ZP probability distribution of activated sludge.

ACTIVATED SLUDGE UNIT DESIGN

Mechanical

Mechanical elements that impact most strongly on the ASU are aeration units and pumps--both have been observed to be a principal cause of process failure through shear of sludge, increasing the detritus, and poor SVI, ZP properties.

Aeration. High-speed aeration and brush aerators used in mixed liquor tanks have been observed to disrupt sludge severely causing the generation of colloidal fines. This upsets the bimodal floc size distribution as previously discussed, and the biopolymer component cannot supply the flocculant capacity to completely reflocculate the detritus into the sludge mass; i.e., the ZP probability curve slope increases because of the colloidal detritus. Low-speed aerators and compressed air systems are alternates that do not have these undesirable properties.

Pumps. High-speed centrifugal pumps and high-pressure drops across valves, etc., wreak havoc on recycled, activated sludge floc. Low-speed recessed impeller, low head pumps have been successfully applied in systems with fairly long aeration tank retention times of 12 hours or more. These long retention times may have contributed to the success by supplying reflocculation time. An attractive sludge recycle system is one used in the municipal sector, air-lift pumps. Since these are low head pumps, proper hydraulics are required and retrofit is not attractive in many existing plants.

Process

Reactor Design. Much has been written about completely mixed and plug-flow reactor designs; completely mixed gaining in popularity over the earlier plug-flow design. Plug flow theoretically yields a slightly better effluent on well-equalized feed streams, and completely mixed systems are less sensitive to some toxic transient loadings.

One area ignored is the role reactor design plays in excess sludge generation; the plug-flow design inherently yields more excess sludge. As an example, Lau (12) recently reported a comparison of results from a completely mixed unit and volumetrically equally sized three-staged reactor completely mixed unit. Treating high-strength, readily biodegradable wastes at various F/M (COD/MLSS) ratios, Lau observed the following waste sludge yields:

F/M	Sludge Yield, Per Cent of Yield for Single Stage Unit at F/M of 0.5	
	Single Stage	Three Stage
0.5	100	150
0.83	400	650
1.0	400	750

These data support the previous discussion that there is a minimum of substrate necessary to maintain cell integrity, active transport, and other mechanical events referred to as maintenance energy. When substrate beyond that needed for maintenance energy is supplied, it is used for cell growth.

Additionally, in the front end of a plug flow or multiple stage system, the microorganisms are exposed to a high concentration of substrate compared to a single stage completely mixed unit. They respond to the increased substrate supply by generating more cell mass. Once the substrate energy has been committed to new cell mass by the microorganisms, most of the commitment is irretrievable and the result is greater sludge production. In aerobic stabilization of waste sludge where some small reduction in cell mass is observed, probably the monomers and polymers in the cell which are the normal building blocks for RNA, DNA, enzymes, peptidoglycan, polysaccharide, and lipid formation that can be salvaged for maintenance energy functions accounts for the loss in mass.

Preferred ASU reactor design for comparatively weak refinery effluent treatment is probably two stage with the lead reactor preferably 80+ per cent of the total reactor volume.

Clarifier Design. A clarifier is usually considered to provide for separation of activated sludge with process design considerations being chiefly overflow and recycle rates. Actually, this is short sighted, and a clarifier design should consider in addition to solid flux rates the elements of: flocculation, capture of solids trapped by surface or interfacial tension, and a stage of reaction. All of these latter elements are provided for in a wide-well clarifier design where the diameter wide well is about one-half the diameter of the clarifier (Figure 10).

It has been well established that gently flocculating activated sludge before clarification improves greatly the sludge settling properties. Flocculation provides for aggregating the fines into the main floc mass and taking advantage of the biopolymers naturally in the system. The wide-well zone provides a region to achieve flocculation, and the improvement in sludge settling more than compensates for the clarifier surface area reduction due to the wide well.

CHEMICAL DESTABILIZATION REQUIREMENTS FOR OPTIMIZING THE PERFORMANCE OF DISSOLVED AIR FLOTATION AND GRANULAR MEDIA FILTRATION UNITS

Addressing water chemistry principles determine the phase separation efficiency of the air flotation and granular media filtration processes. Fundamentally, maximizing phase separation efficiency by the air flotation process requires recognizing that an intrinsic property of solids in the presence of water is a negative, electrical-surface charge (zeta potential). Flotation air bubbles also have a negative zeta potential as does the surface of granular media in a filter. Maximizing phase separation efficiency requires that these coulombic repulsive forces be controlled by controlling the properties of the dispersed phase (13).

Air Flotation and Granular Media Filtration Definitions

A proper place to start a discussion of air flotation is a definition that recognizes the principal limitation of the process; it will not efficiently achieve the phase separation of colloidal solids. The definition, therefore, should spell out the application more carefully than done heretofore:

> Dissolved air flotation may be defined as clarification of a suspension of flocculated material by contact with minute bubbles that attach to the solids constituting the suspension causing the suspensions to be separated from the clarified water by flotation.

The definition puts proper emphasis on the fact that the material being separated should not be colloidal with its inherent high, repulsive, negative zeta potential required to maintain the colloidal state, but a flocculated suspension. A flocculated suspension implies a proper chemical pretreatment consistent with the needs of a colloidal system.

Similarly:

> Granular media filtration may be defined as clarification of a suspension of dispersed material by passage through a bed of porous media that separates and retains within the media the solids constituting the suspension.

Properties of Suspended Solids

Refinery effluents from aerated lagoons are similar to surface waters, API separator effluents, fire, and cooling water ponds, etc., in that the suspended materials usually are predominately colloidal or a combination of colloidal and very slightly flocculated suspensions. The stability of these colloidal systems relates to the fact that the individual particles carry like electrical charges causing their mutual repulsion. Except for some isolated examples, the charge on organic, inorganic, and biocolloids is negative when suspended in water. Colloidal destabilization by chemical treatment has the objective of neutralizing or reducing the electrical charge so that mutual repulsion is reduced to the extent that individual particles can approach each other close enough for van der Waals and/or chemical forces to become effective. The attractive van der Waals' forces cause the particles to aggregate into agglomerates which facilitate their removal by sedimentation, air flotation, or filtration processes. The surface charge on colloidal particles may be estimated by electrophoretic, electroosmotic, streaming, and sedimentation potential techniques.

We have found that the electrophoretic procedures and equipment of Riddick (14) permits the rapid determination of colloidal charge to be made and all our investigations involved use of Zeta Meter. Accordingly, electrokinetic values reported herein are zeta potentials (ZP).

Electrokinetic Charge on Colloidal Particles

Microorganisms, dispersed oil colloids, and inert suspended matter such as inorganic sulfides, silt, coke fines, etc., that are present in refinery effluents are negatively charged.

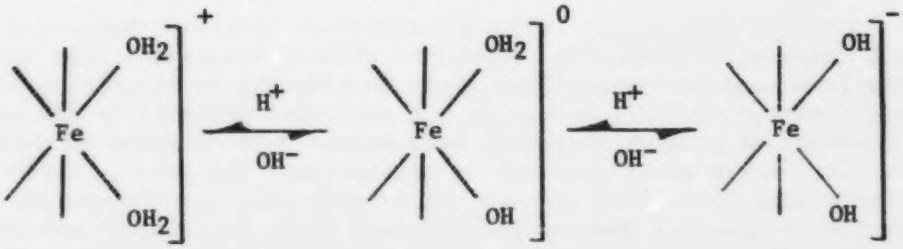
The efficiency of air flotation for phase removal depends on the state of subdivision of the suspended matter; higher capture and removal efficiencies are achieved with discrete particles of substantial size, and increasingly poorer efficiencies are observed with increasing colloidal solids fraction. Investigation revealed that the negatively-charged flotation microbubble was repulsed by the negatively-charged colloidal solids such that poor bubble adherence for flotation occurred. Consequently, the key to maximizing the effectiveness of the air flotation process was found to be essentially neutralizing or reducing the electrical charge of the colloidal particles to eliminate the coulombic repulsion due to like charges.

Source of Charge. The net electrokinetic charge, i.e., zeta potential, on colloidal particles is a result of (1) ionization, (2) ion adsorption, and (3) ion dissolution mechanisms.

The amino acids, proteins, and polysaccharides constituting the surface of biocolloids, for example, acquire their charge mainly through ionization of functional carboxyl and amino groups to give $-COO^-$ and $-NH_3^+$ ions. The degree of ionization of these functional groups and, thereby, the net charge on the particle depends on the pH of the solution. The pH at which the ZP is zero is called the isoelectric point; at a lower pH, the ZP is positive, and at a higher pH, it is negative.

Solids dispersed in water typically have negatively-charged surfaces because cations have a greater tendency to become hydrated and reside in the aqueous solution than do anions which are smaller, less hydrated, and more polarized, thereby having the greater tendency to be adsorbed. The net surface charge, i.e., ZP, may be acquired by the unequal adsorption of oppositely-charged ions; however, ion adsorption may be positive or negative.

Ionic substances may acquire a surface charge because the ions of which they are composed dissolve unequally in solution. In the case of the aluminum and iron primary coagulants, for example, hydrogen and hydroxyl ions are in equilibrium with the solid phase hydrous oxide. With excess hydrogen ions, the surface of the solid phase is positively charged with excess hydroxyl ion; the surface is negatively charged. Since the concentrations of the hydrogen and hydroxide ions determine the chart at the particle surface, they are called potential determining ions. This concept may be illustrated as follows:



As early as 1879, Helmholtz (13) described the charge on colloidal surfaces in terms of an "electric double layer" and, subsequently, Guoy and Chapman (14) described a diffuse electric double layer model that permitted more quantitative treatment of electrokinetic data. Verwey and Overbeek (15) set forth the classic work containing the mathematical foundation for showing that the tendency of fine particles to remain dispersed was due to the mutual repulsion of their electrical double layers being sufficient to overcome the van der Waals' attractive forces pulling them together. The Russian investigators, Landau and Derjaguin, had much the same idea and published the electrical double-layer repulsion part in 1941. The total treatment is now known as the DLVO Theory (16).

Electric Double Layer. The electric double layer may be regarded as consisting of two regions: (a) an inner region which may include adsorbed ions and (b) a diffuse region in which ions are distributed according to electrical forces and thermal motion.

Stern (17) proposed a model in which the boundary of the inner region (Stern layer) was located by a plane (the Stern plane) about a hydrated ion radius from the surface. Adsorbed ions attached to the surface by electrostatic and/or van der Waals' forces may be dehydrated in the direction of the surface. A certain amount of solvent will also be bound to the charged surface in addition to the adsorbed ions. The shear plane, therefore, is probably located farther from the surface than the Stern plane. Ions with centers beyond the Stern plane are considered to be in the diffuse part of the double layer. These concepts are illustrated in Figure 11.

Electrokinetic potentials relate to the mobile part of the particle, therefore, the electrokinetic unit consists of the volume enclosed by the shear plane which is rather inexactly known. The potential difference between the surface of shear and the solution is called the zeta potential (ZP).

Colloid Destabilization Mechanisms

Destabilization of the waterborne suspended solids may involve four mechanisms: (1) colloid entrapment or removal via the sweep floc mechanism, (2) reduction in surface charge by double-layer repression, (3) charge neutralization by adsorption, and (4) bridging by polymers.

Colloid Entrapment. Colloid entrapment involves chemical treatment with comparatively massive amounts of primary coagulants; the amount of coagulant used is typically so great in relation to the amount of colloidal matter that the nature of the colloidal material is not relevant. The amount of primary coagulant used may be 5 to 40 times as much as is used for charge neutralization by adsorption. The rate at which the primary coagulants form hydrous metal oxide polymers (Figure 12) is relatively slow and depends chiefly upon water temperature and pH. Coupled with the high concentration used, all negatively-charged colloidal material is initially exposed to charge neutralization by the transient cationic species. The polymer matrix is 3-dimensional and voluminous as illustrated by Figure 13, providing for entrapment of solids. As the polymer contracts, freeing solvent water molecules and settles, the suspended solids remain enmeshed in the settling floc and appear to be swept from the water; hence, the description of the process as a "sweep floc" mechanism. This destabilization mechanism can result in the generation of large amounts of wet alum (or iron) sludges which are difficult and costly to dewater. Even though it is by far the most widely used mechanism for water clarification, it is not recommended because of the sludge problem and because the use of other mechanisms result in significantly lower operating and capital costs.

Double-Layer Repression. Reduction in surface charge by double-layer repression is caused by the presence of an indifferent electrolyte which in refineries is chiefly sodium chloride from brackish water usage or salt water ballast. For water and monovalent electrolytes, the thickness of the double layer is as follows:

Thickness of Double Layer, Angstroms	NaCl Concentration		Specific Cond., Micromhos
	M	mg/l	
1,000	.00001	0.6	-
600	-	1.0	-
320	.0001	6	-
230	-	10	25
100	.001	59	115
75	-	100	200
32	.01	585	1,000
23	-	1,000	1,900
10	.1	-	8,800
7.3	-	10,000	15,000

For double-layer repression of colloid surface charge in brackish waters, the sodium ions of the indifferent electrolyte which surrounds the colloid particles in order to electrically balance their negatively-charged surfaces have less tendency to diffuse away from the colloid surface as the salinity increases. Some salt concentration may eventually be reached such that the thickness of the double layer may be small enough that two colloids approach each other closely enough that van der Waals' forces cause aggregation. An important aspect of double-layer repression is that the quantity of colloidal charge is not significantly reduced but just the extent to which it extends out from the colloid surface. This relates to the nature of the destabilizing chemical (salt) and its mode of action; i.e., the sodium ions remain free in the solvent and cause rapid dissipation of the charge as the distance from the colloid surface increases.

The above-mentioned principles can be visualized by the representations of the double layer in demineralized, fresh, brackish (or salt) waters illustrated in Figure 14, 15, and 16 respectively.

For demineralized water there are not many ions available; therefore, the charge on the particle surface is not reduced much by adsorbed ions in the Stern layer or counter-ions in the diffuse layers. As a result, the zeta potential is high and extends for a considerable distance into the solvent; i.e., the double layer is thick.

Fresh water, on the other hand, comparatively may contain many salts. As illustrated, the presence of counter-ions may lead to some adsorption and potential drop across the Stern layer. The concentration of counter-ions in the diffuse layer is much greater than the demineralized water example and causes the charge to dissipate more rapidly; i.e., the double layer is much thinner than the demineralized water example.

In the example for brackish or salt water, the comparatively high concentrations of sodium ions discourages their diffusion away from the particle surface. The counter-ions occupying the Stern layer cause an apparent reduction in potential but are not strongly adsorbed and, therefore, do not permanently alter the surface potential charge to the much lower charge of the Stern potential and the charge actually measured, the zeta potential. The high electrolyte concentration causes any residual charge to dissipate rapidly; i.e., the double layer is very thin.

Charge Neutralization. Charge neutralization by adsorption of the destabilizing chemical to the colloid is a key mechanism for optimizing removal of waterborne solids from brackish waters by direct filtration. The colloidal charge may not only be reduced to zero, but beyond zero, i.e., reversed. Charge neutralization by adsorption infers that the colloid-water interface is changed and, thereby, its physicochemical properties. It doesn't require much extension of one's imagination to see how this destabilization mechanism can explain those cases where optimal chemical dosages were found and overdosing resulted in a deterioration in, or failure of, direct filtration. This phenomenon is more typically experienced using very low molecular weight polyelectrolytes or surfactant-type molecules with little bridging properties. Some examples of charge neutralization mechanisms are shown schematically in Figure 17.

Bridging. Bridging by organic and inorganic polymers describes the destabilization mechanism where the molecules of the added chemical attach onto two or more colloids causing aggregation. There are two kinds of bridging; polyelectrolyte bridging between dissimilarly and similarly charged materials. An example of the first kind is the bridging of negatively-charged colloids by cationic polyelectrolyte. Because of the coulombic atraction involved, this destabilization is not difficult to perceive. On the other hand, weakly anionic organic polymers are negatively charged; however, they are especially useful for aggregating and binding together some negatively-charged aggregates into agglomerates that resist redispersion. Thus, in this instance, attractive forces of a chemical nature seem to overcome electrostatic repulsion forces due to like charges. An electrical model proposing a mechanism for this seeming anomaly has been offered by Grutsch and Mallatt (18). Bridging by polymers proved to be an important destabilization mechanism for optimizing phase removal processes.

DLVO Theory

The DLVO Theory quantifies particle stability in terms of energy changes when particles approach one another. The total energy is determined by summation of the attraction (London-van der Waals' forces) and repulsion (overlapping of electric double layers) energies in terms of interparticle distance. The general character of the resulting interaction energy-distance curve illustrates the very significant conclusions: 1) attraction will predominate at small and large distances and 2) repulsion may predominate at intermediate distances depending on the actual values of the two forces. An important purpose of the chemicals used for destabilization is to reduce or eliminate the repulsion force at intermediate distances so that attractive forces will predominate and the particles will aggregate.

These principles are readily illustrated by the interaction energy curves in Figure 18. The energy of attraction curve (V_a) and the energy repulsion curve (V_r) are summed and yield the interaction energy curve (V_t). The interaction energy curve shows a repulsive energy maximum (V_m) which is an energy barrier to coagulation and the formation of stable aggregates of particles by attainment of interparticle distances which permit attractive forces at the primary minimum to react. This example illustrates another characteristic feature of these energy curves and that is the existence of a secondary minimum at relatively large interparticle distances. If this secondary minimum is moderately strong, it can give rise to a loose, easily-reversible form of flocculation. For small particles with a diameter less than about 200 A^o, the secondary minimum cannot achieve this loose, reversible flocculation in those cases where the energy barrier (V_m) is large enough to prevent normal coagulation into the primary minimum. Thus, for complete destabilization of systems composed of fine particles, a chemical approach that responds to zeta potential charge neutralization is required.

A graphic illustration of how zeta potential charge neutralization leads to destabilization is illustrated in Figure 19. Letting V_{R1} be the energy of repulsion curve for the particle system, summation of V_{R1} with the energy of attraction (V_a) gives the curve for the energy of interaction (V_{T1}). This curve demonstrates that a repulsion always exists which accounts for the stability of the original colloidal system.

The effect of adding an increment of chemical which reduces the zeta potential by charge neutralization is illustrated by summing the new energy of repulsion curve (V_{R2}) with V_a which yields the energy of interaction curve V_{T2}. This curve has the secondary minimum which provides for loosely-flocculated aggregates as previously described for Figure 18. However, an energy barrier still exists which precludes flocculation of particles smaller than 200 A° diameter.

Further addition of chemical which lowers the energy of repulsion curve to that described by V_{R3} yields the interaction curve V_{T3} when summed with V_A. This interaction curve has a large secondary minimum, no repulsion barrier, thus, all particles are coagulated into aggregates by the attraction energy of the primary minimum.

Double-layer repression, therefore, can improve solids removal by direct filtration, but this mechanism does not achieve the best results and can conceal definition of optimal chemical pretreatment to achieve best filtration results if the interference of this destabilization mechanism is not recognized. Our refinery experience indicates that the colloidal aggregates destabilized by double-layer repression appears analogous to loose flocculation by the secondary minimum and the aggregates are readily redispersed by hydraulic forces as if the net binding forces are very weak. A simple procedure to identify the existence of the double-layer repression mechanism in brackish waters so that it can be avoided and optimized chemical treatment can be achieved has been described (19).

Destabilizing Chemicals

Primary Coagulants. Efficient destabilization of colloidal suspensions using salts of iron and aluminum as primary coagulants must recognize the properties of these primary coagulants. The chief properties of concern are the ZP-pH relationships and hydrolytic reactions.

Stumm and O'Melia (20) describe the equilibrium composition of solutions in contact with precipitated primary coagulants in the interesting manner shown in Figures 20 and 21. These diagrams are calculated using constants for solubility and hydrolysis equilibria. The shaded areas, A and B, we have added in each figure are approximate operating regions for air flotation and clarifiers by colloid entrapment (region A) and direct filtration by charge neutralization (region B). Both regions are assumed to cover a pH range of 6.0 to 8.5. The coagulant dosage ranges from 33 to 200 mg/l in region A and 3.3 to 20 mg/l in region B. These figures are useful in the interpretation of some of our filtration and air flotation unit results.

With reference to Figure 21, the isoelectric point for ferric hydroxide coincides with the region of minimum solubility, and the operating regions for water treatment (destabilization) yield a hydrolyzed, primary coagulant with a desirable positive zeta potential.

In many refinery situations, however, it is difficult to use this attractive condition because the presence of sulfides and strongly reducing conditions cause the reduction of ferric to ferrous iron and the formation of mixed iron sulfides with no coagulation powers. In fact, in some refinery waters, the use of iron coagulants at modest dosages may contribute to stabilizing solids rather than destabilizing them.

While alum has no redox or sulfide chemistry comparable to iron, its amphoterism and solubility pose definite limitations on alum usage. With reference to Figure 20, a substantial portion of operating region B lies in the area where alum is soluble and the predominant equilibrium species is negative, $Al(OH)_4^-$. In the more acidic part of region B, however, the concentration of equilibrium ionic species is very much lower and much less negative. Considering these data, it is not unexpected that investigators consistently report optimal coagulation/flocculation results with alum at a pH of 5-6.

With inspection of Figure 20, one may question why alum is effective at all for neutralizing negatively-charged colloids in the indicated operating regions. One approach to explaining observed performance requires understanding that the data are equilibrium data; but before equilibrium is reached, substantially different conditions exist.

Alum very readily hydrolyzes to form polymers in a complex manner not well defined. The hydrolytic pathway and reaction rates are affected by pH, temperature, other ions, etc. One hypothesized route which includes different aluminum hydrolysis products which are known to exist is outlined in Figure 12. When alum is added to water in amounts which exceed the solubility limits, sequential kinetic reactions occur until the ultimate precipitate is formed and the ionic species appropriate to the pH equilibrate with the precipitate. The hydrolytic reactions are formed which are available for colloid adsorption. The hydrolyzed species have enhanced adsorption capabilities, possibly due to larger size and less hydration and the presence of coordinated hydroxide groups (20). In solutions more alkaline than the isoelectric point, the positively-charged polymers are transient and at equilibrium, anionic polymers prevail.

In modestly alkaline solution, the transient positively-charged polymers appear to contribute to destabilization of colloids. On the other hand, in solutions more acidic than the isoelectric point, the positively-charged polymers prevail at equilibrium and destabilization of colloids may be achieved at significantly lower coagulant treatment levels.

In Figure 22, the zeta potentials of colloidal iron hydroxide solutions are plotted as a function of pH. The zeta potential decreases in positive charge as the pH increases until the isoelectric point is reached at the pH of 8.3 at which the charge reverses. In the vicinity of the isoelectric point, the charge may vary as indicated. Alum has a similar zeta potential-pH relationship as shown in Figure 23. The zeta potential may be negative or positive over the pH range of 7.0 to 7.8.

Salts appear to interfere with the coagulative powers of alum by anion penetration of the alum polymer by chloride ion. Anion penetration, the replacement of a coordinated group such as aquo, hydroxo, or another anion, can be visualized with reference to Figure 12. Chloride ion is a highly mobile, nonhydrated, electronegative ion that at high concentrations penetrates the hydrous aluminum oxide polymer, impairs the olation of alum to polymers, and reduces the formation or charge of the transient cationic alum polymers which are very important to colloid charge reduction.

Surfactants. Certain substances, even when present in very low concentrations, possess the unique property of altering the surface energy of their solvents to an extreme degree. Almost always, a lowering rather than an increase of the surface energy is affected. Substances or solutes possessing such properties are known as surface-active agents or surfactants and their unique effect is known as surface activity.

By broad definition then, surface-active chemicals are soluble substances whose presence in solution markedly changes the properties of the solvent and the surfaces they contact. They are categorized according to the manner in which they dissociate or ionize in water and are characterized structurally by possessing a molecular balance of a long lipophilic, hydrocarbon "tail" and a polar, hydrophilic "head."

Surfactants owe their physicochemical behavior to their property of being adsorbed at the interface between liquids and gases (where they contribute to the electrical charge on the DAF bubble) or liquid and solid phases (where they may contribute to the zeta potential). Surfactants tend to concentrate in an oriented manner, at the interface, in such a way that almost entirely, they turn a majority of their hydrophilic groups toward the more polar phase and a majority of their lipophilic groups away from the more polar phase and, perhaps, even into a nonpolar medium. The surface-active molecule or ion, in a sense, acts as sort of a bridge between two phases and makes any transition between them less abrupt.

There are three types of chemical surface-active agents which are classified according to their dissociation characteristics in water. These are:

1. Anionic Surfactants--Where the electrovalent and polar hydrocarbon group is part of the negatively-charged ion when the compound ionizes:

ANIONIC $CH_3(CH_2)_{16}COO^-Na^+$

2. Nonionic Surfactants--Where the hydrophilic group is covalent and polar and which dissolves without ionization:

NONIONIC $CH_3(CH_2)_{16}COO(CH_2CH_2O)_xH$

3. Cationic Surfactants--Where the electrovalent and polar hydrocarbon group is part of the positively-charged ion when the compound ionizes:

CATIONIC $CH_3(CH_2)_{17}NH_3^+CL^-$

Surfactants are powerful charge neutralizers (and charge reversers). In the petroleum industry, anionic surfactants are used as emulsifiers for asphalt by imparting a zeta potential on asphalt particles ranging from -30 to -80 mV. Cationic types impart a zeta potential ranging from +18 to 128 mV. Each surfactant possesses a distinct characteristic capability of imparting quantitatively to asphalt during emulsification, a specific zeta potential.

Surfactants have not found wide use for destabilizing colloidal systems. In fact, they are an important cause for the existence of colloidal systems, particularly in primary municipal effluents. The principal organic colloidal destabilizing chemicals are polyelectrolytes.

Polyelectrolytes. Polyelectrolytes used as water-treating chemicals are macromolecules having many charged groups and may be classified as cationic, anionic, and nonionic depending upon the residual charge on the polymer in solution. Examples of the structural types are shown in Table 1.

In solution, the polyelectrolytes are dissociated into polyvalent macroions and a large number of small ions of opposite charge (counter ions). The macroion is highly charged, which is the cause for the characteristic properties of the polyelectrolytes. Most of the macroions are long, flexible chains, their size and shape depending on the macroion charge and interaction with counter ions. With increasing charge, the macroion extends; with decreasing charge, the macroion assumes a contracted random coil. The source of the charge is illustrated by the polyacrylates, a widely-used polymer. In distilled water, polyacrylic acid's carboxylic functional group is only slightly dissociated. The addition of NaOH reacts with the carboxylic acid groups causing them to dissociate leaving a charge on the macroion and producing sodium counter-ions as shown in Figure 24.

The Dimensions Involved. The dimensions of the various components involved in colloid destabilization vary a million fold, from a few A° to more than 10 A° as shown in Table 2.

Where color is not a significant factor, the problem is usually one of causing colloidal particles down to about 1000 A^o in diameter to aggregate. When a clarifier or DAF is used for phase separation, it is desirable to build aggregates to fairly large size, say greater than 10^6 A^o. On the other hand, when filters are used, simply destabilizing the colloidal particles is sufficient because the destabilized particles will build aggregates in the filter bed as the destabilized suspension passes through the media and the particles impinge and adhere to the media or trapped suspended matter.

Systematic Approach to Determining Chemical Treatment Requirement

Broad experience in refinery effluent treatment led to outlining the condition response schematic for chemical treatment of waterborne colloids shown in Figure 25. In phase removal by filtration, or even DAF, we are not concerned with, and indeed it is desirable to avoid, the use of (1) the "sweep floc" of colloid entrapment and (2) the double-layer repression mechanisms for colloid destabilization. Destabilization efforts must focus on the charge neutralization and bridging mechanisms. Charge neutralization correlated with plant performance as the optimum destabilization mechanism. For plant control of direct filtration, charge neutralization has been the key test parameter correlating with performance of refinery filters. Brackish water required that charge neutralization be measured after dilution with distilled water to separate the effects of double-layer repression and charge neutralization; i.e., under plant conditions of high salinity, the addition of destabilization chemicals could reduce the ZP to approximately zero by a range of chemical treatments; however, when double-layer repression was the cause of reduced ZP, reduced filter run lengths and performance were observed. Reducing the ZP to approximately zero, as measured by means responsive to charge neutralization, point out more definitively the required destabilization chemical treatment and resulted in optimum filter performance.

Waterborne colloids subject to chemical destabilization and phase separation fall into two general categories: relatively inert substances such as clays, sand, and organic materials; and microorganisms or biocolloids. Both categories of colloidal matter may be stabilized because they are charged and/or are highly hydrophilic. Both categories of colloidal matter also may vary in response to treatment by destabilization chemicals and within each category, the state of subdivision seems to require additional consideration; i.e., extremely small colloidal particles are sometimes more difficult to aggregate for removal by filtration. Typically, destabilization of biocolloids, such as are in aerated lagoon effluents, is a more demanding problem.

In the case of polyelectrolytes, some counter ions at high concentrations screen the charged functional groups with an ionic cloud as previously described. Salinity, hydroxide, phenolics, sulfides, etc., are examples of the kinds of counter ions found to affect various cationics. Each waste water application of cationics must address the contaminants present if the most cost-effective polyelectrolyte is to be used (21).

PROPOSED CHEMICAL AND BIOLOGICAL DESTABILIZATION MODELS

Anionic polyelectrolytes are frequently used to flocculate negatively-charged colloidal systems. Even better acknowledged is the capability of the activated sludge process to flocculate negatively-charged sewage and industrial colloidal systems; an extreme case being the Contact Stabilization variation of the activated sludge process. Because the activated sludge mass and the anionic polyelectrolytes are both negatively charged, both of these destabilization examples seem to be counter to theory. A possible explanation for these extremely valuable properties lies in their electrical characteristics and the environment in which they operate.

Electrical Characteristics of Polyelectrolytes

As discussed previously ionizable groups on the polyelectrolyte are the source of an electric field. Neglecting the effect of counter ions, the field about an extended polyelectrolyte is shown qualitatively in Figure 26. In this example, there are potential maxima in the region of the charged functional groups. There is a lesser potential field, outside the region of potential maxima, that might be described as a "potential tunnel." This is illustrated isometrically in Figure 27. When the polyelectrolyte is in the random coil conformation as shown in Figure 28, there is an additional weak potential region (B) in the polyelectrolyte's sphere of influence. A fourth potential region is the solution where there is no potential effect due to the polyelectrolyte.

Each potential region has a different effect on counter ions. In the three potential regions within the polyelectrolyte's sphere of influence, counter ions can be considered as being bound to the polyelectrolyte. In the region of potential maxima, the bound counter ion may be localized at charged functional groups forming ion pairs. In the potential tunnel region, the bound counter ions are mobile, as they are in the weak potential region. Mobile counter ions establish an equilibria, therefore, between the potential tunnel, weak potential field in the sphere of influence, and the solution. An especially unique property of polyelectrolytes is that the bound counter ions in the potential tunnel area can move parallel to the polyelectrolyte molecule in the apparent volume occupied by the potential tunnel; thus, counter ions can "flow" in the potential tunnel areas of Figures 27 and 28 analogous to water in a garden hose. Polyelectrolyte solutions, therefore, show an extremely large dielectric constant.

The dielectric constant or polarizability of polyelectrolytes is determined by the volume of polyelectrolyte in which counter ions are retained (not by the charge density of the polyelectrolyte) as long as a region of bound but mobile counter ions is formed. The dielectric increment depends on the geometry of the polyelectrolyte; extended polyelectrolytes give much larger dielectric increments than polyelectrolytes in the random coil conformation. Further, the dielectric increment of polyelectrolytes in the extended (or helix) conformation increases rapidly with increasing length. Uniform and continuous distribution of charged groups and the mobility of bound counter ions are essential for large polarizability (22).

Polyelectrolyte Destabilization Model

The means for negatively-charged polyelectrolytes to destabilize negatively-charged colloids is hypothesized to lie in the electrical properties of the polyelectrolyte. The proposed model in Figure 29 illustrates, approximately to scale, the colloid, its electrical double layer, the anionic polyelectrolyte, and its potential tunnel. Counter ions are cations in both cases.

Cations in the double layer are subject to at least two opposing electrical forces, coulombic attraction to the colloid particle and, also, to the solvent to maintain an electrically-balanced system.

When the sphere of influence of the anionic polyelectrolyte approaches the electrical double layer of the colloid, repulsion due to encountering like charges might be expected. However, in this instance, apparently:

1. The polyelectrolyte's electrical sphere of influence shields the counter ions in a localized area of the colloid double layer from the attractive, electrical solvent forces.

2. The resulting electrical imbalance results in an increase in the negative coulombic potential in the localized area on the colloid.

3. The increase in negative coulombic potential attracts the mobile counter ions from the potential tunnel region of the polyelectrolyte.

4. The potential tunnel of the polyelectrolyte serves as a conduit for counter ions which neutralize the surface charge in the localized area of the colloid surface.

5. The charge neutralization achieved reduces the energy of repulsion at the localized site sufficiently so that the sum of the energy of repulsion and energy of attraction curves yields an interaction energy of attraction at the localized site (Figure 18).

6. The positive interaction energy at the localized site permit attractive London-van der Waals' forces at the primary minimum between the polyelectrolyte and colloid to react.

The key to this hypothetical model is the mechanism by which the anionic polyelectrolytes implement the initial shielding action of the colloid surface from the electrical solvent forces. This capability lies in the special properties of the polyelectrolyte: polarizability, bound but mobile counter ions in the potential tunnel, and equilibria between counter ions in the potential tunnel and sphere of influence established by coulombic forces.

Repulsion due to like coulombic charge is illustrated in Figure 30. In Figure 30A, the double layer overlap for energy of repulsion curves A (polyelectrolyte) and B (colloid) result in a net repulsion indicated by curve C. If this were a system of lyophobic colloids, it would be a stable colloidal system. Polyelectrolytes are extremely polarizable, however, particularly the high molecular weight anionics. The polarizing polyelectrolyte can supply an essentially infinite quantity of counter ions via its potential tunnel to a localized site near a colloid particle. This influx of counter ions reduces the repulsion energy curve A by double-layer repression because of the equilibria established by the bound mobile counter ions, and the surfaces can approach more closely as shown in Figure 30B. The influx of counter ions to the localized charged region between the polyelectrolyte and colloid surface also would be expected to reduce the energy of repulsion (curve B) for the colloid in the localized region. The distance between the charged surfaces can be diminished further for this additional reason as illustrated in Figure 30C.

Interaction between the two surfaces is achieved at localized sites if the counter ions reduce the energy of repulsion curves such that the energy of interaction curve provides for a secondary minimum (see Figure 18). Particles larger than about 200 A° are flocculated. Further reduction in the energy barrier of the repulsive energy maximum permits flocculation of the particles less than 200 A°.

Sterically, when the two surfaces approach closely as illustrated in Figure 30C, the polyelectrolyte provides a shielding or insulating effect to the localized colloid site from the coulombic solution forces. Negating the effect of solution forces results in an increase in attraction of counter ions to be localized colloid site and contributes further to polyelectrolyte polarization and double-layer charge repression at the site.

Electrical Characteristics of Microorganisms

The microorganisms constituting activated sludge also have a negative zeta potential. Glucuronic acid has been proposed as the source of the electrical charge.

As shown in Figure 31, the outermost surface of most bacteria is a slimy capsule varying in thickness up to 100,000+ A°. The capsule composition varies with species and may consist of polymers of glucose or other sugars, amino and acid sugars, or polypeptides. Capsules generally consist of about 98 per cent water. The function of the capsular layer is proposed as serving the microorganisms as an osmotic barrier, i.e., a mechanism for guarding against too rapid an influx or efflux of water (23). We propose that the capsular layer performs an equally if not more important function of providing the potential tunnel region.

The zeta potential is the charge difference between the plane of shear and the solution. In the case of microorganisms the shear plane is some small, but indeterminate distance beyond the outer boundary of the capsule. It is hypothesized that the region beyond the shear plane is analogous to the diffuse layer of counter ions in the colloid double-layer model (Figure 11), whereas the capsule on the capsule side of the shear plane serves a function analogous to the potential tunnel region of polyelectrolytes; i.e., it provides for a region of bound, but mobile counter ions. The acidic polysaccharides in the outer layer of the soft layer are at least partially responsible for the negative, electric charge on the bacteria surface. As in the polyelectrolyte example, mobile counter ions establish an equilibria between the capsule layer (potential tunnel) and the solution and the bound counter ions in the capsule layer can move parallel to the cell wall of the microorganism. The chief difference between the polyelectrolyte potential tunnel and the biological potential tunnel (capsule) is the comparatively large volume of the capsule-a desirable property.

Biological Destabilization Model

As for polyelectrolytes, the means for negatively-charged microorganisms to destabilize negatively-charged colloids also is hypothesized to lie in the electrical properties of the microorganisms. The model proposed for polyelectrolytes (Figure 29) is analogous to the model for the biological system. Once again, cations are counter ions in both cases. Dimensionally, the activated sludge floc and the capsule volume are larger than the comparative volumes occupied by the polyelectrolyte and its potential tunnel at the very low concentrations of polyelectrolyte used (frequently less than 1 mg/1). As the diffuse counter ion layer of the double layers overlap (Figure 30A), compared to polyelectrolytes, the massive size of the microorganisms floc more readily shields the counter ions in the colloid double layer from coulombic solvent forces. The microorganisms supply counter ions to satisfy the electrical imbalance from their potential tunnel (capsule). The localized increase in counter ions reduces the energy of repulsion curve analogous to anionic polyelectrolytes and the particles flocculate.

The new technology, which is the subject of this article, forms the basis for a number of U.S. and foreign patent applications. Williams Brothers Waste Controls, Incorporated, of Tulsa, Oklahoma, has been licensed to employ this technology and to sublicense others throughout the world.

BIOGRAPHY

James F. Grutsch is Coordinator, Environmental Projects, Standard Oil Company (Indiana). He holds undergraduate and graduate degrees in chemistry from Indiana University. Prior to his present assignment with Standard, Jim served successively as Group Leader for finishing, blending and reclamation at the Amoco Oil Whiting refinery, and Coordinator of Waste Disposal for Amoco. Jim taught undergraduate chemistry for six years at Indiana.

BIOGRAPHY

Russell C. Mallatt is Manager, Environmental & Energy Conservation, Standard Oil Company (Indiana). He holds degrees in chemistry from the University of Illinois and the University of Rochester. Prior to his present assignment with Standard, Russ served successively as Chief Chemists, Chief Process Engineering and Technical Services Superintendent of the Amoco Oil refinery at Whiting, Indiana.

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DISCUSSION

Milton Beychok, Consulting Engineer: Isn't the optimum sludge age for the PAC addition related to equilibrium capacity of carbon? Why recycle spent carbon?

Grutsch: It doesn't seem to work that way, Milton. It seems to work as a sequential operation with some bioregeneration of the PAC. First, the biological organisms appear to reduce the TOC/COD to a low level, and second, the carbon then takes over and reduces the residual TOC/COD to even lower levels as a direct function of carbon surface area. Bioregeneration of carbon surface seems to be indicated. For example, at soluble TOC levels of 25 mg/l in an activated sludge control unit, a parallel unit with 2,500 mg/l PAC sees 25/2,500 or 0.01 lb. TOC/lb. PAC at start-up, but at 100 days sludge age the equilibrium exposure is 1 lb. TOC/lb. PAC at 24 hours retention time and increases with dilution rate. To achieve TOC reductions at these loadings in this concentration range is not expected, therefore, some of the PAC surface area must be bioregenerated to supply more surface area which, of course, supplies more driving force for TOC reductions.

Experiments with active carbons with different surface areas indicates equilibrium carbon surface area in the activated sludge unit determines effluent quality (at fixed activated sludge unit operating conditions); the larger the surface area, the lower the concentration of residual substrates.

George Reid, O.U. Professor: When you go to a long-term retention time, don't you increase the capital and operating cost?

Grutsch: If by "long-term retention time" you mean high sludge age--the answer for low and moderate strength wastewater typical of refineries is no, you actually can decrease costs. An extended discussion of the advantages of high sludge age activated sludge units with their required pretreatment for reducing capital and operating costs is included in our paper in the Proceedings of the First Open Forum on Management of Petroleum Refinery Wastewaters.

Reid: Unless I misunderstood, is there a possibility of using a low sludge age system?

Grutsch: I think that is the wrong way to go. It is the wrong way to go because low sludge age systems maximize the conversion of the organic substrate to biological solids (see Fig. 7). You don't want to do that because of the dewatering and disposal costs. You want to remove them chemically, since the art is available to remove them chemically. And second, a front end biological system such as a trickling filter does not remove the troublesome colloidal fraction that ruins the activated sludge electrical properties so that you can cycle up to high sludge age. I think chemical engineering principles properly applied here give maximum returns in better effluent quality at lower operating and capital costs.

Bob Carloni, Lion Oil Company: Do I understand from your discussion that to flocculate a negatively charged colloid, one should use an anionic polyelectrolyte in preference to a cationic?

Grutsch: I don't want you to close your mind to that possibility. For example, you can use a two-chemical or a one-chemical system. With the proper facilities, a two-chemical system may be cheaper. Using a two-chemical system in a municipal plant, the addition of an anionic polyelectrolyte at 0.3 to 0.5 mg/l to the influent of the primary clarifier dramatically improves the removal of most of the suspended matter. The residual colloidal material can then be destabilized more economically by cationic polyelectrolyte charge neutralization for essentially complete removal in a following DAF or granular media filter. By contrast, a one-chemical system involves use of only a cationic polyelectrolyte for charge neutralization and bridging. One-chemical systems may be more costly in chemical requirement than a two-chemical system.

John Penniman, Pen Kem, Incorporated: The paper industry, using the dissolved air flotation process under careful zeta potential control, has reduced particulate concentration from a save-all to well under 10 ppm. Bearing in mind that zeta potential can fluctuate in refinery effluent, even after equalization, from-6mV to-18mV, and that automatic zeta potential instrumentation is now available, would you speculate on its applicability to improving the reliability and economics of water clarification.

Grutsch: Well, that is hard for me to put into perspective. We like to follow the KISS principle; that is, "keep it simple, stupid!" So we don't like to put too big a demand on the plant personnel. For example, in chemical addition we would like the plant operator only to look at the chemical addition pump to determine if the pump is running and pumping, and that is all he has to concern himself about.

So we use the zeta potential determinations to screen various polyelectrolytes and look for a polyelectrolyte that is insensitive to the system that we are trying to destabilize. Then we try to pick a treatment concentration where the suspended solids or pH variation doesn't significantly change the chemical dosage. There will be sensitive systems that might use feed-back control. Of course, if the chemical prices increase inordinately, we will have to get a little bit more conservative in our use and that might pay off a feed-back control system.

TABLE 1. EXAMPLES OF CATIONIC, NONIONIC AND ANIONIC POLYELECTROLYTES

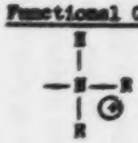
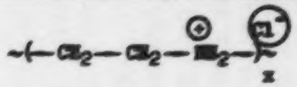
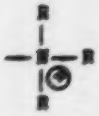
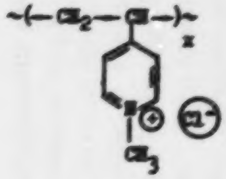
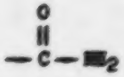
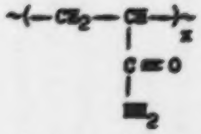
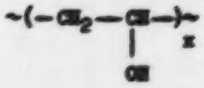
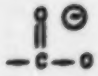
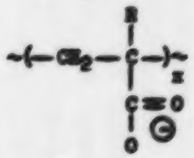
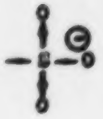
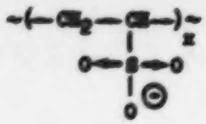
Polyelectrolyte Description	Structural Type	Functional Group	Example	
Cationic	Amines			Polyethylenimine Hydrochloride
	Quaternary			Poly(N-methyl-4-vinyl pyridinium chloride)
Nonionic	Polyamide			Polyacrylamide
	Polyalcohol	$-OH$		Polyvinylalcohol
Anionic	Carboxylic			Poly(meth)acrylic Acid
	Sulfonic			Polyvinylsulfonate

TABLE 2. DIMENSIONS INVOLVED IN COLLOID DESTABILIZATION

		DIAMETER, ANGSTROMS
A.	SOME COLLOIDAL SYSTEMS	
	COLOR BODIES	50 - 1000
	INERT COLLOIDS (CLAY, SILT, INORGANIC SALTS, ETC.)	1,000 - 30,000
	EMULSIONS	2,000 - 100,000
	BACTERIA	5,000 - 100,000
	ALGAE	50,000 - 8,000,000
B.	CATIONS	
	Na^+	1.9
	Ca^{++}	2
	Mg^{++}	1.3
	Al^{+++}	1
C.	POLYELECTROLYTES	
	POTENTIAL TUNNEL	7-11
	CHAIN LENGTH, 100,000 - 15,000,000 M.W.	250,000 - 40,000,000
D.	ELECTRICAL DOUBLE LAYER	
	RANGE OF EXPECTED VALUES	5-100
	EXPECTED TYPICAL IN REFINERY	30
E.	SOLVENT	
	H_2O	

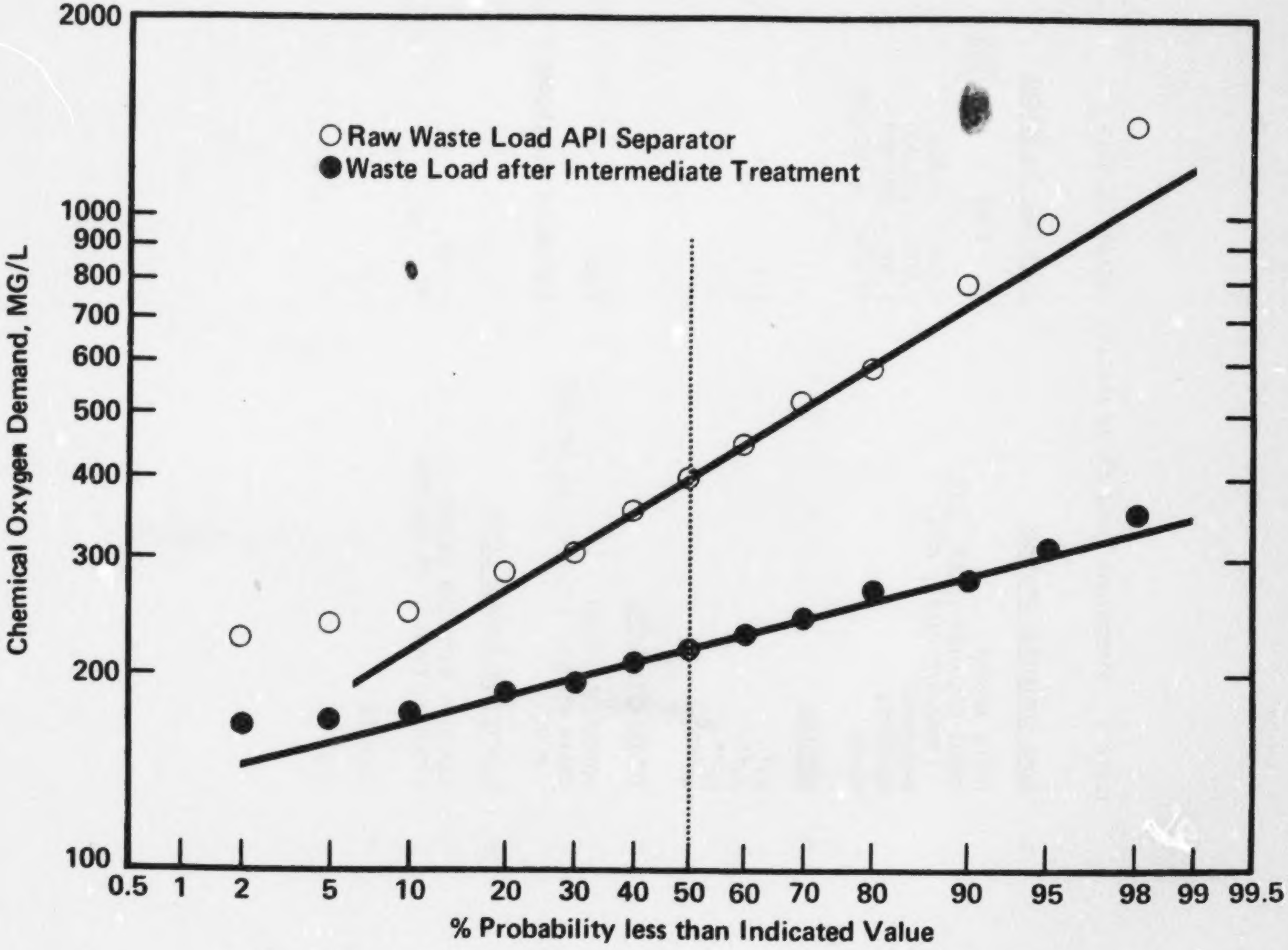


Fig. 1 Probability Plots of COD Before and After Intermediate Treatment

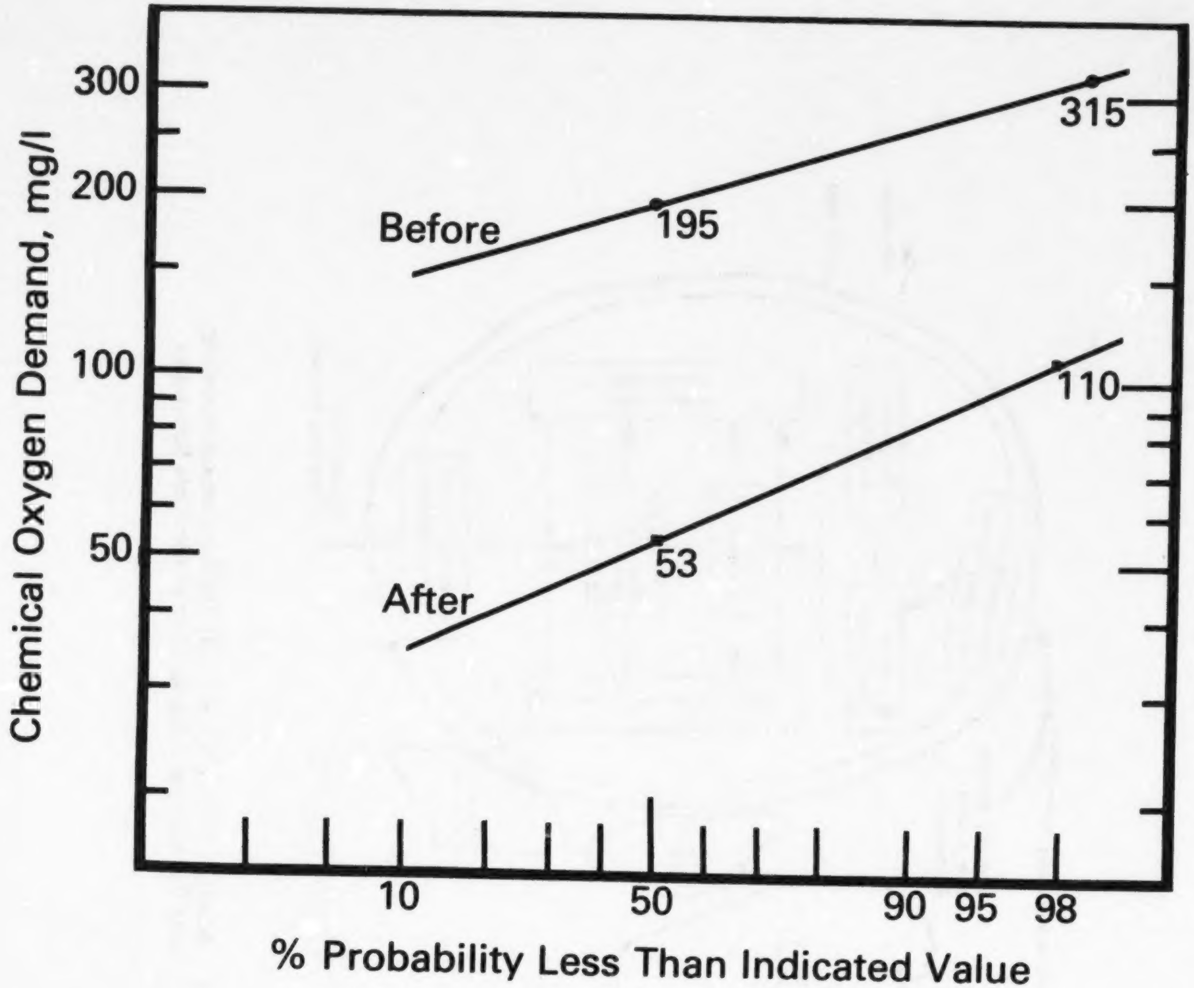


Fig. 2 Primary Municipal Effluent - Before And After Filtration (WPCF, V.48 #7, p.1801)

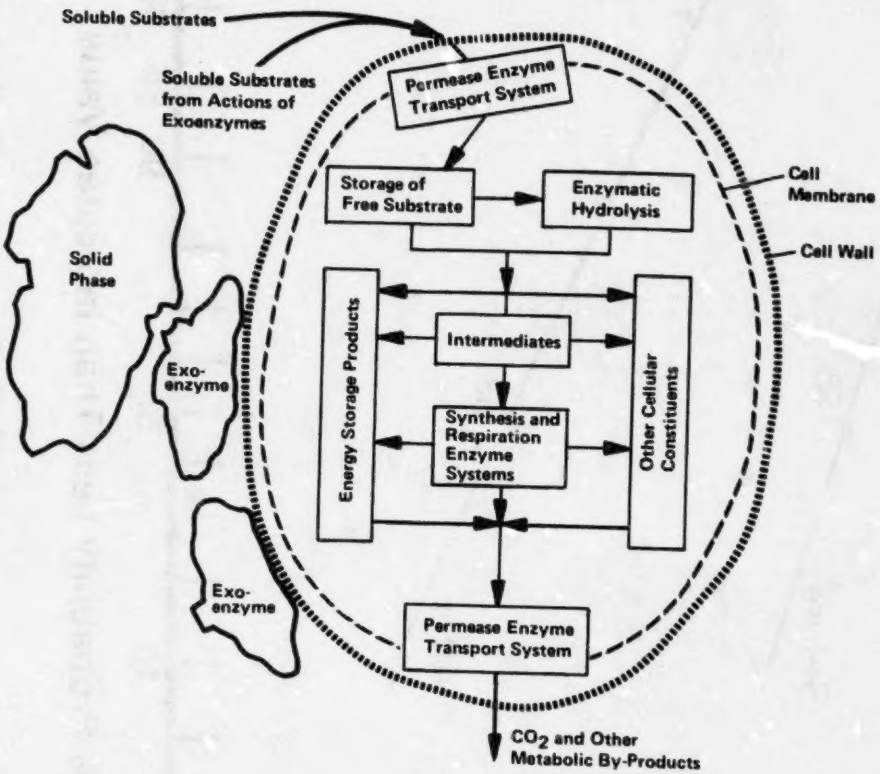
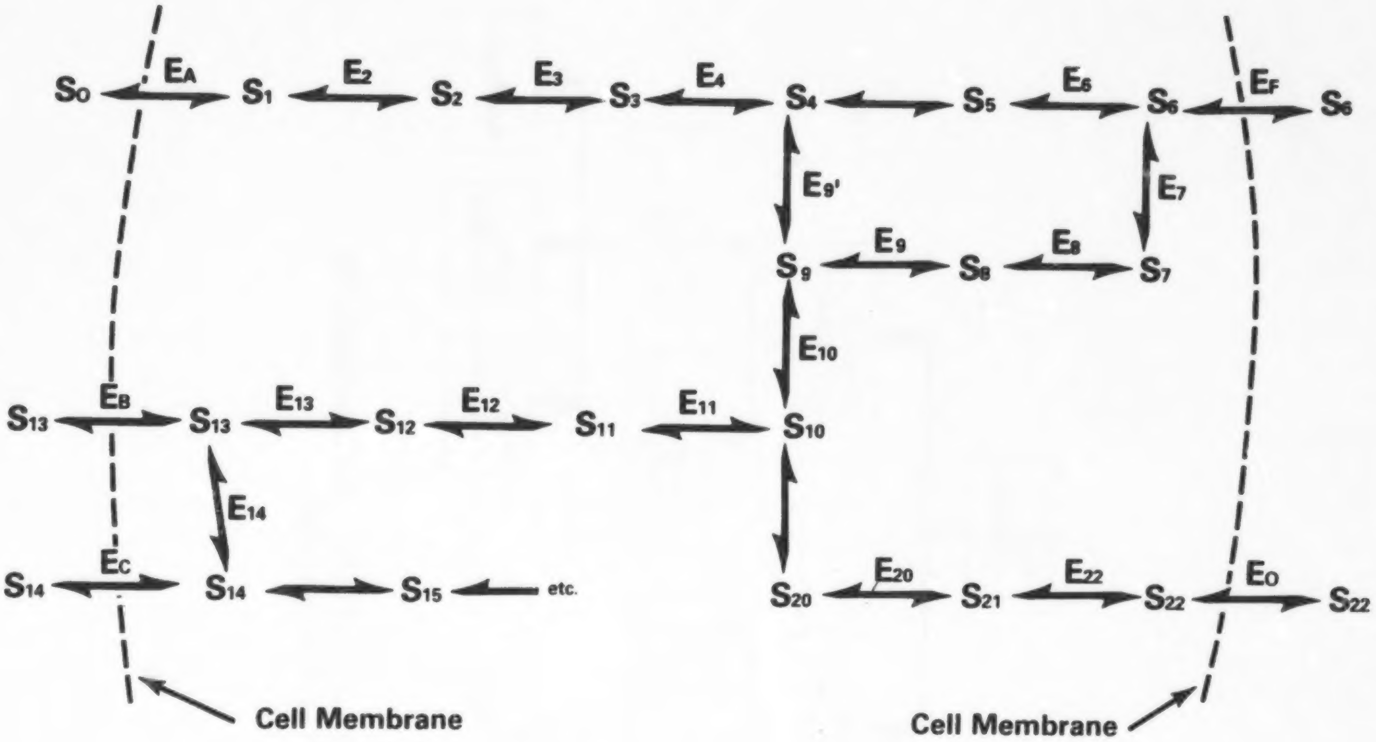

Soluble Substrates
Soluble Substrates from Actions of Exoenzymes
Permease Enzyme Transport System
Storage of Free Substrate
Enzymatic Hydrolysis
Cell Membrane
Cell Wall
Solid Phase
Exo-enzyme
Energy Storage Products
Intermediates
Other Cellular Constituents
Synthesis and Respiration Enzyme Systems
Exo-enzyme
Permease Enzyme Transport System
CO$_2$ and Other Metabolic By-Products

Fig. 3 Schematic of a Bacterial Cell, Its Biochemical Activities, and Exoenzyme Solubilization of Insoluble Substrates



S_O, S_1, S_2, etc. — Organic molecules
E_A, E_B, E_c, etc. — Enzyme transport systems
E_1, E_2, E_3, etc. — Endoenzymes

Fig. 4 Sequential Endoenzyme Biological Oxidation Showing Permease Active Transport

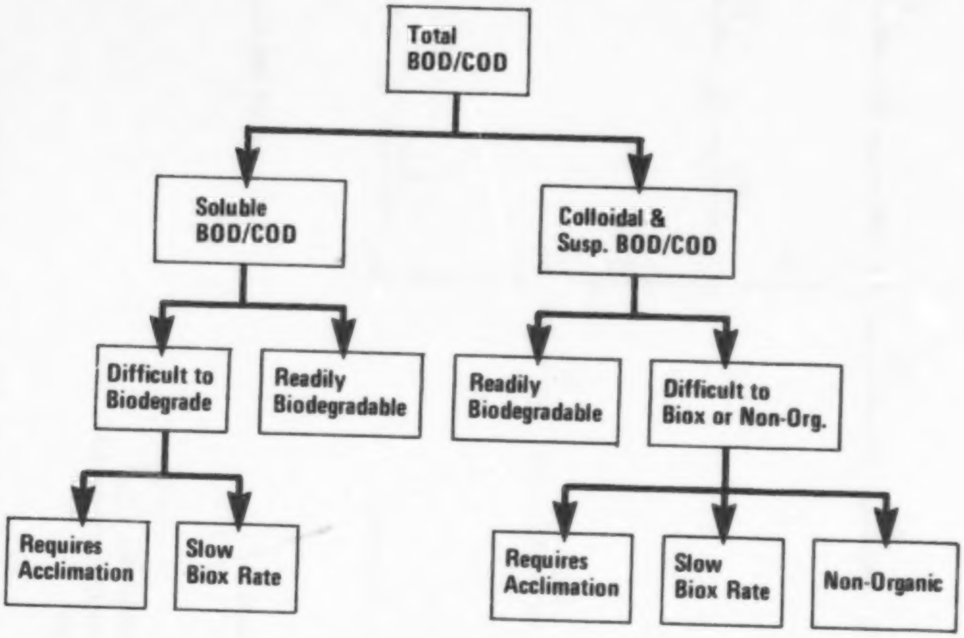


Fig. 5 Impacts of BOD/COD Components On Activated Sludge Unit

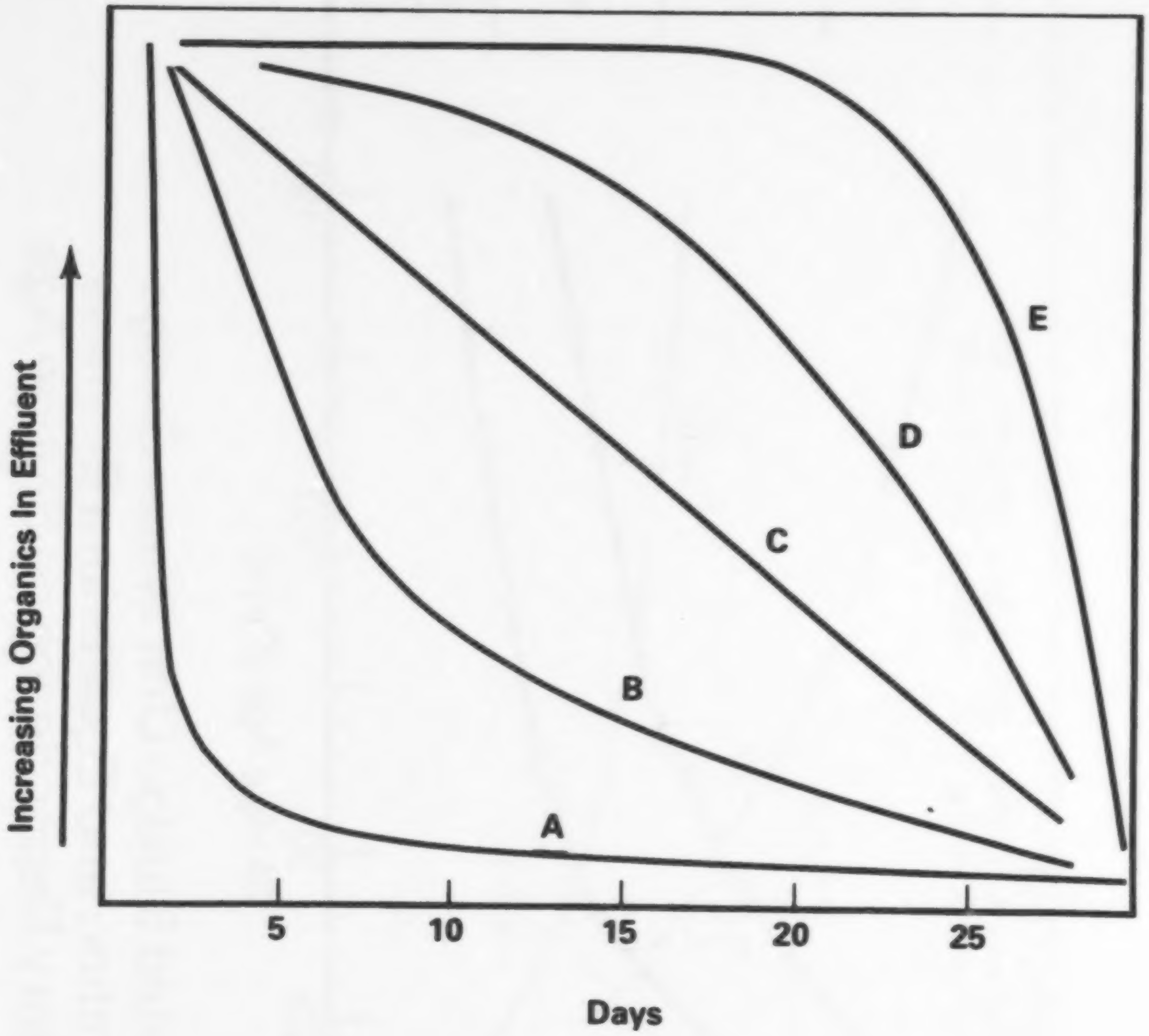


Fig. 6 Biological Removal Of Contaminants With Time--Types Of Removal Curves

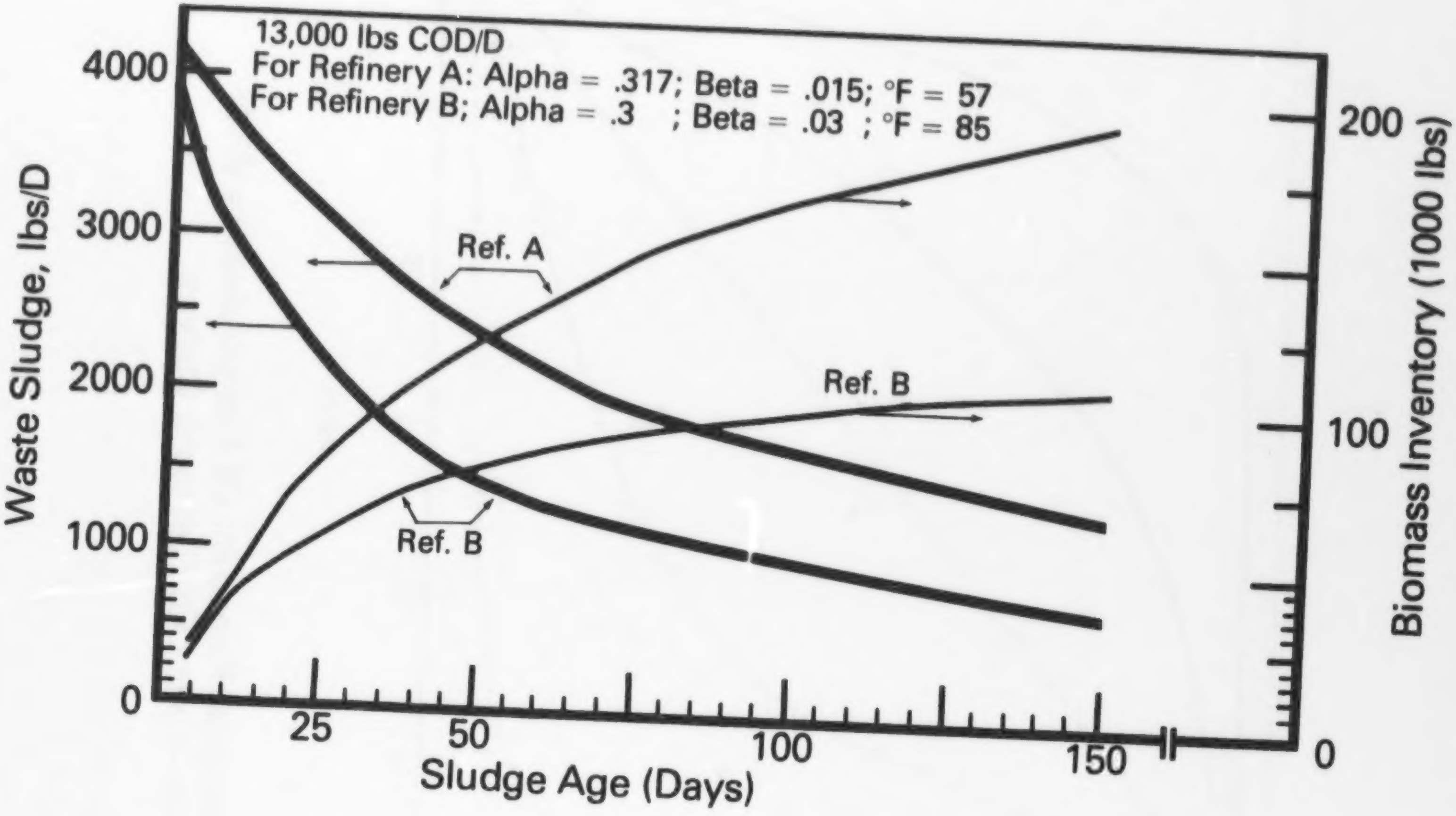


Fig. 7 Activated Sludge Unit Waste Sludge Generation and Equilibrium Biomass Inventory Dependence on Sludge Age

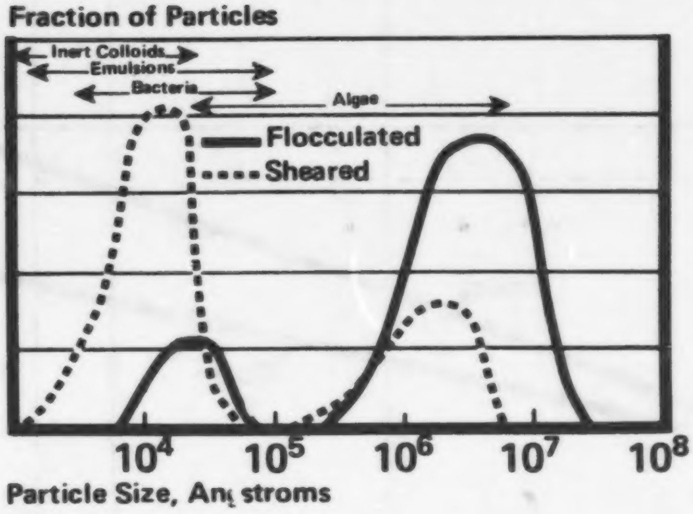


Fig. 8 Activated Sludge Bimodal Floc Size Distribution

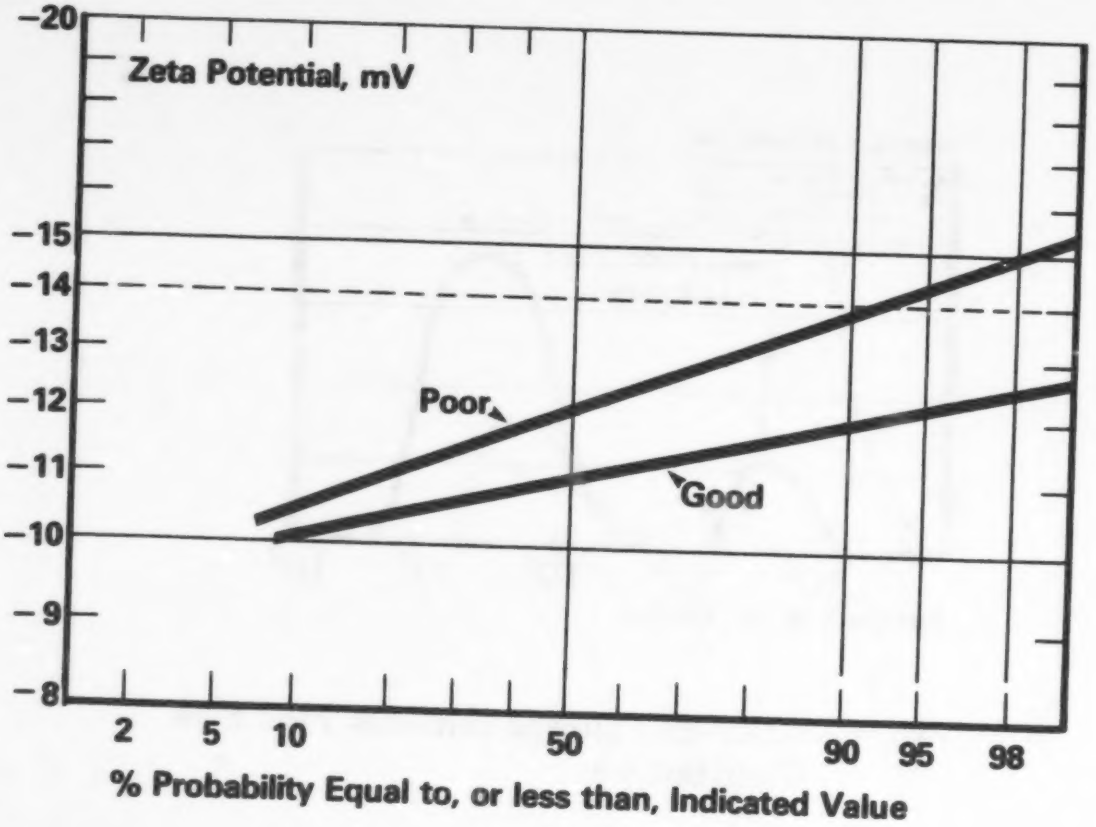


Fig. 9 Zeta Potential - Probability Curves for Poor and Good Settling Activated Sludges

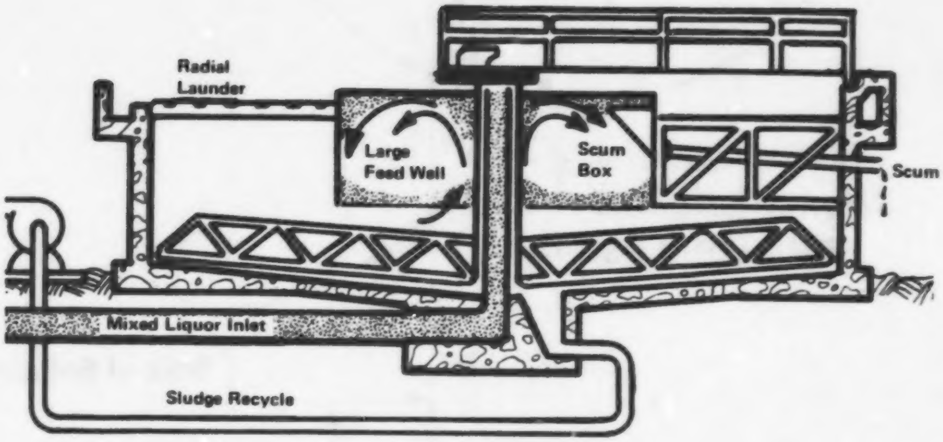


Fig. 10 Wide Well Clarifier

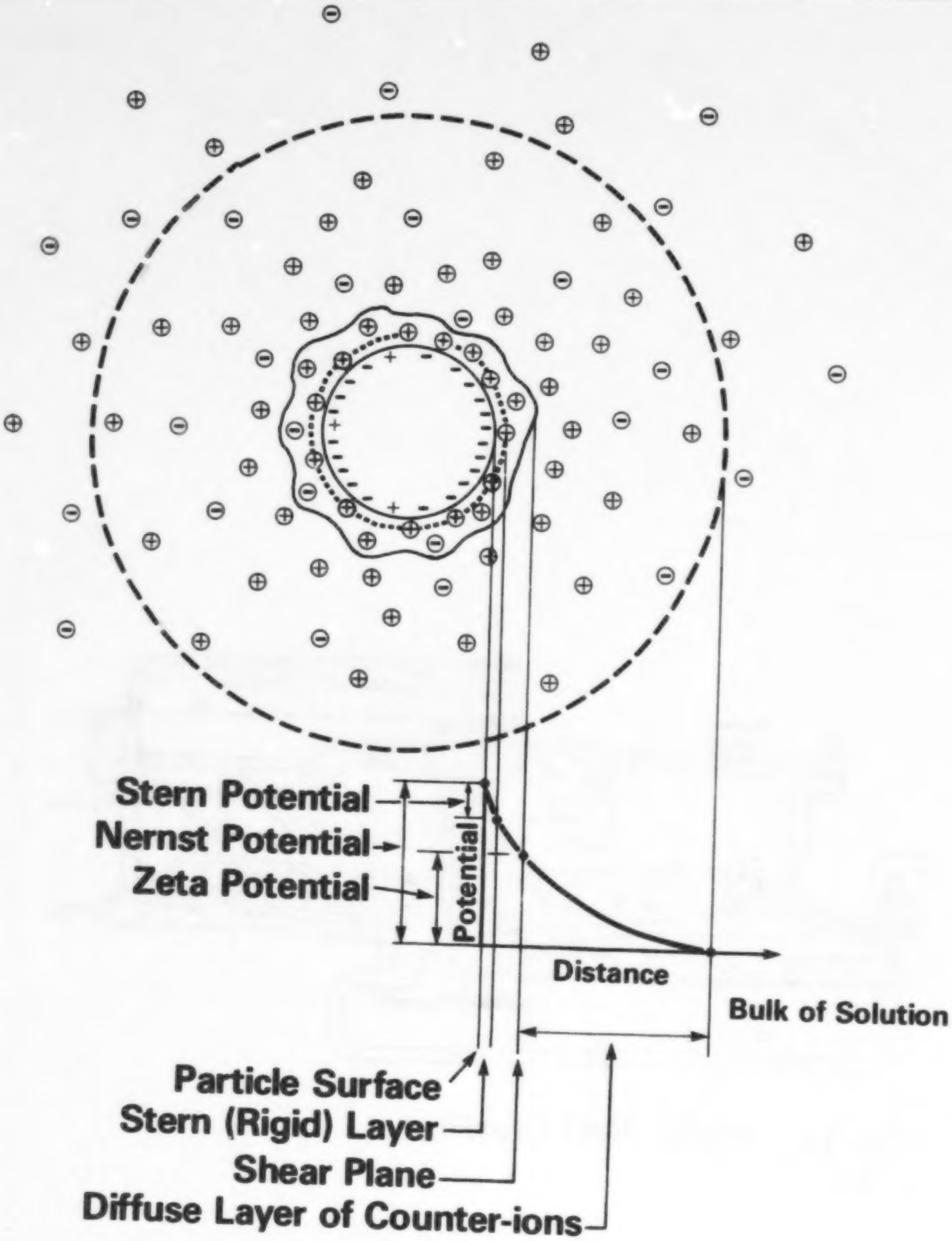


Fig. 11 Representation of Electric Double Layer According to Stern's Theory

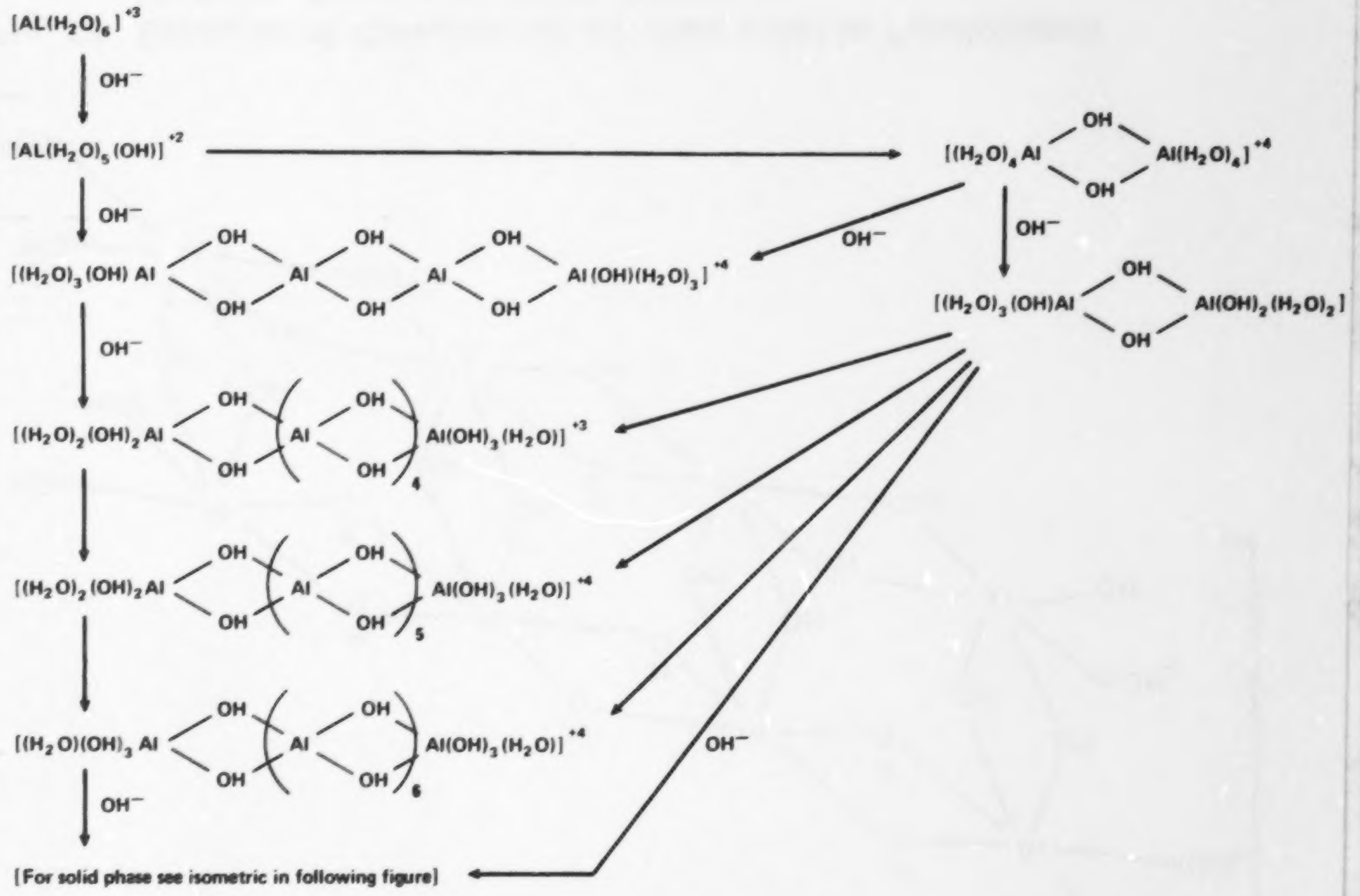

$[AL(H_2O)_6]^{+3}$
OH^-
$[AL(H_2O)_5(OH)]^{+2}$
$[(H_2O)_4Al$ OH OH $Al(H_2O)_4]^{+4}$
OH^-
$[(H_2O)_3(OH)Al$ OH OH $Al(OH)_2(H_2O)_2]$
OH^-
$[(H_2O)_3(OH)Al$ OH OH Al OH OH Al OH OH $Al(OH)(H_2O)_3]^{+4}$
OH^-
$[(H_2O)_2(OH)_2Al$ OH OH Al OH OH $_4$ $Al(OH)_3(H_2O)]^{+3}$
$[(H_2O)_2(OH)_2Al$ OH OH Al OH OH $_5$ $Al(OH)_3(H_2O)]^{+4}$
$[(H_2O)(OH)_3Al$ OH OH Al OH OH $_6$ $Al(OH)_3(H_2O)]^{+4}$
OH^-
OH^-
[For solid phase see isometric in following figure]

Fig. 12 Sequential Formation of Hydrous Aluminum Oxide Polymers

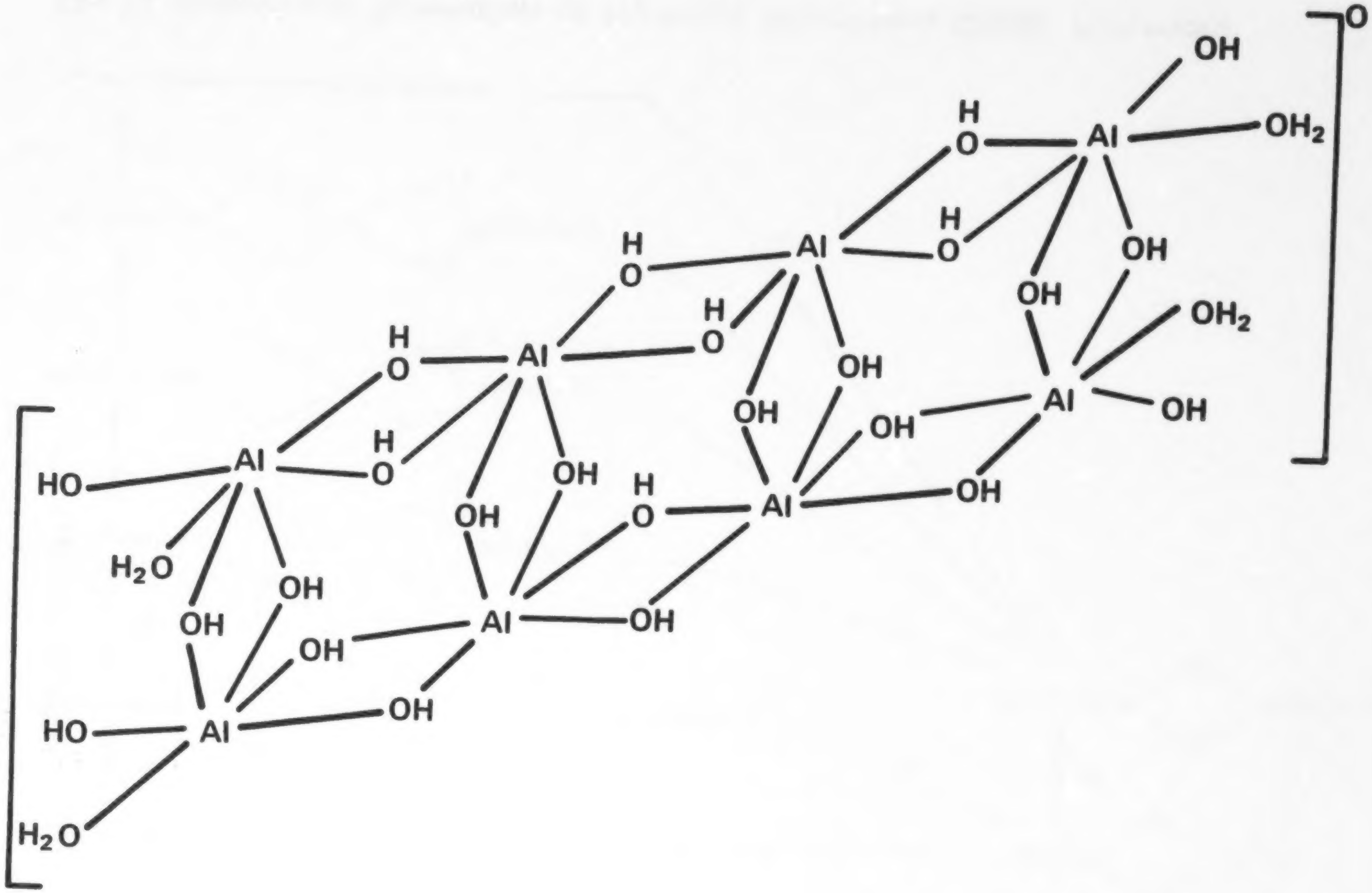


Fig. 13 **Example of Complex which may exist in Precipitated Hydrous Aluminum Oxide Polymers**

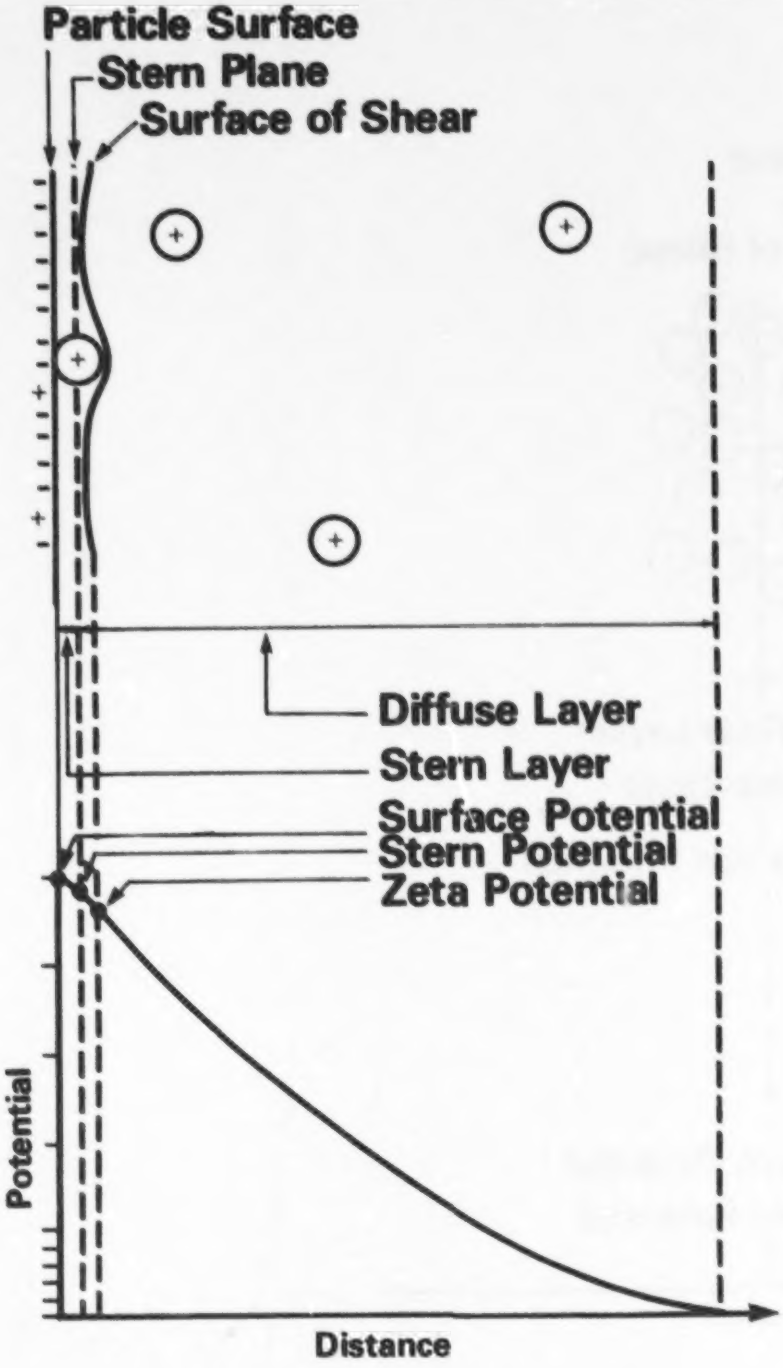


Fig. 14 Representation of Electric Double Layer in Demineralized Water

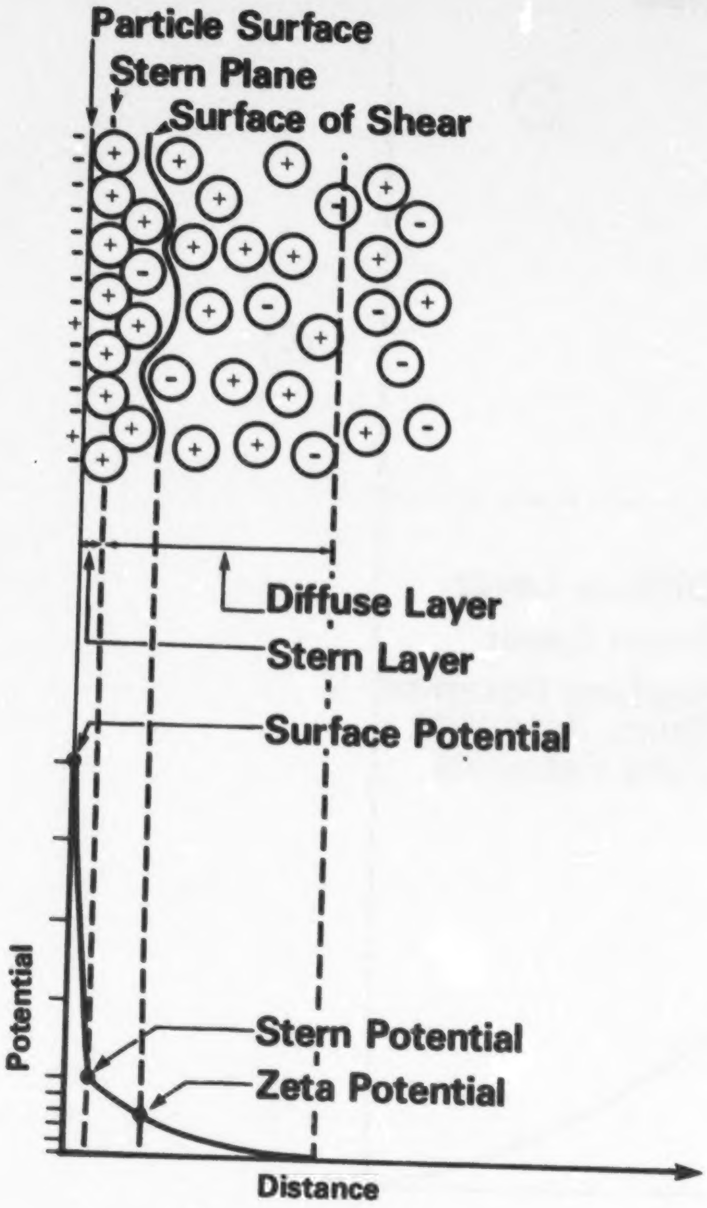


Fig. 16 Representation of Electric Double Layer in Brackish Water

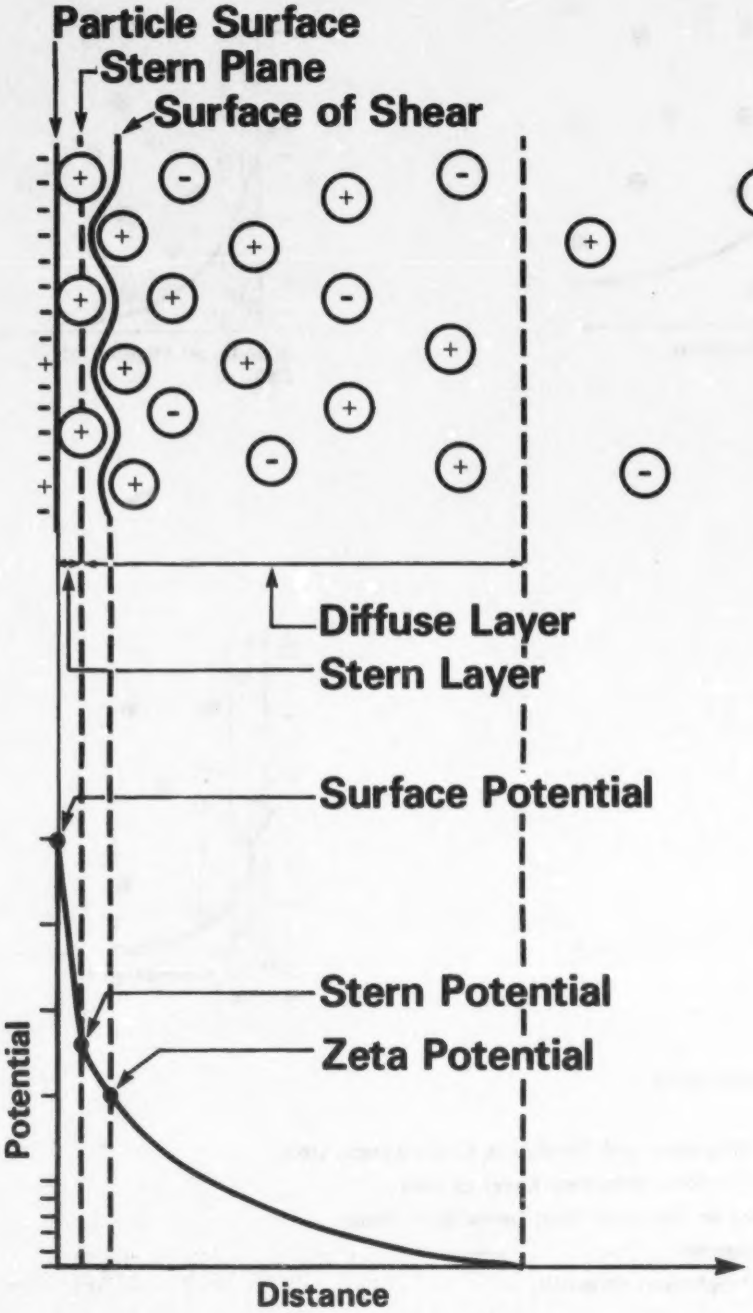
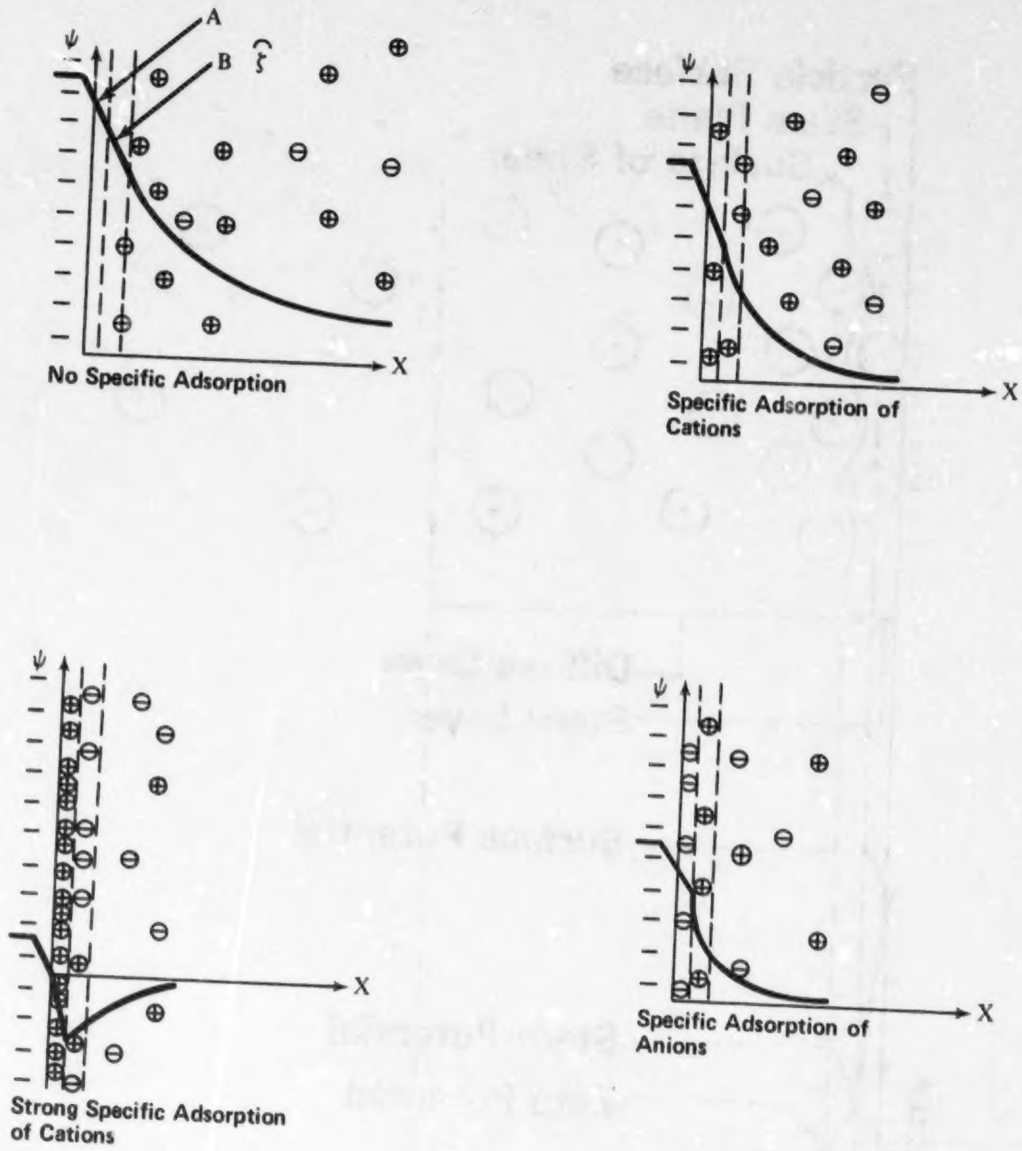


Fig. 15 Representation of Electric Double Layer in Fresh Water



No Specific Adsorption

Specific Adsorption of Cations

Strong Specific Adsorption of Cations

Specific Adsorption of Anions

A	Rigid Layer Migrating with Particle as Single Kinetic Unit
B	Slipping or Frictional Boundary Layer of Ions
X	Distance from an Arbitrary Point Inside Solid Phase
ψ	Electrical Potential
ζ	Zeta or Electrophoretic Potential

Fig. 17 Distribution of Ions and Potentials in the Double Layer Surrounding Colloids (After Overbeek 8)

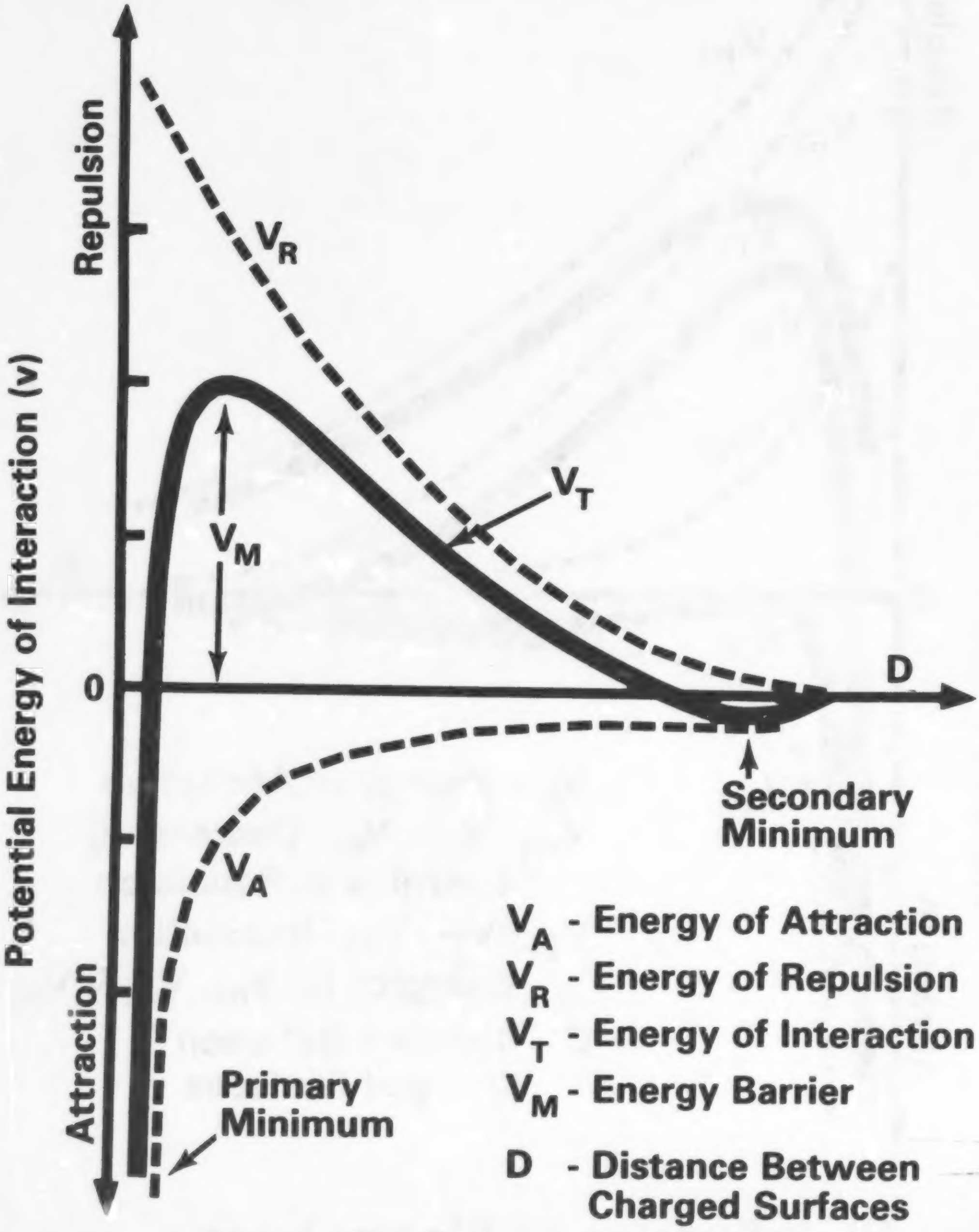

Repulsion
Potential Energy of Interaction (v)
Attraction
0
V_R
V_T
V_M
D
Secondary Minimum
V_A
Primary Minimum
V_A - Energy of Attraction
V_R - Energy of Repulsion
V_T - Energy of Interaction
V_M - Energy Barrier
D - Distance Between Charged Surfaces

Fig. 18 Potential Energy of Interaction for Two Charged Surfaces

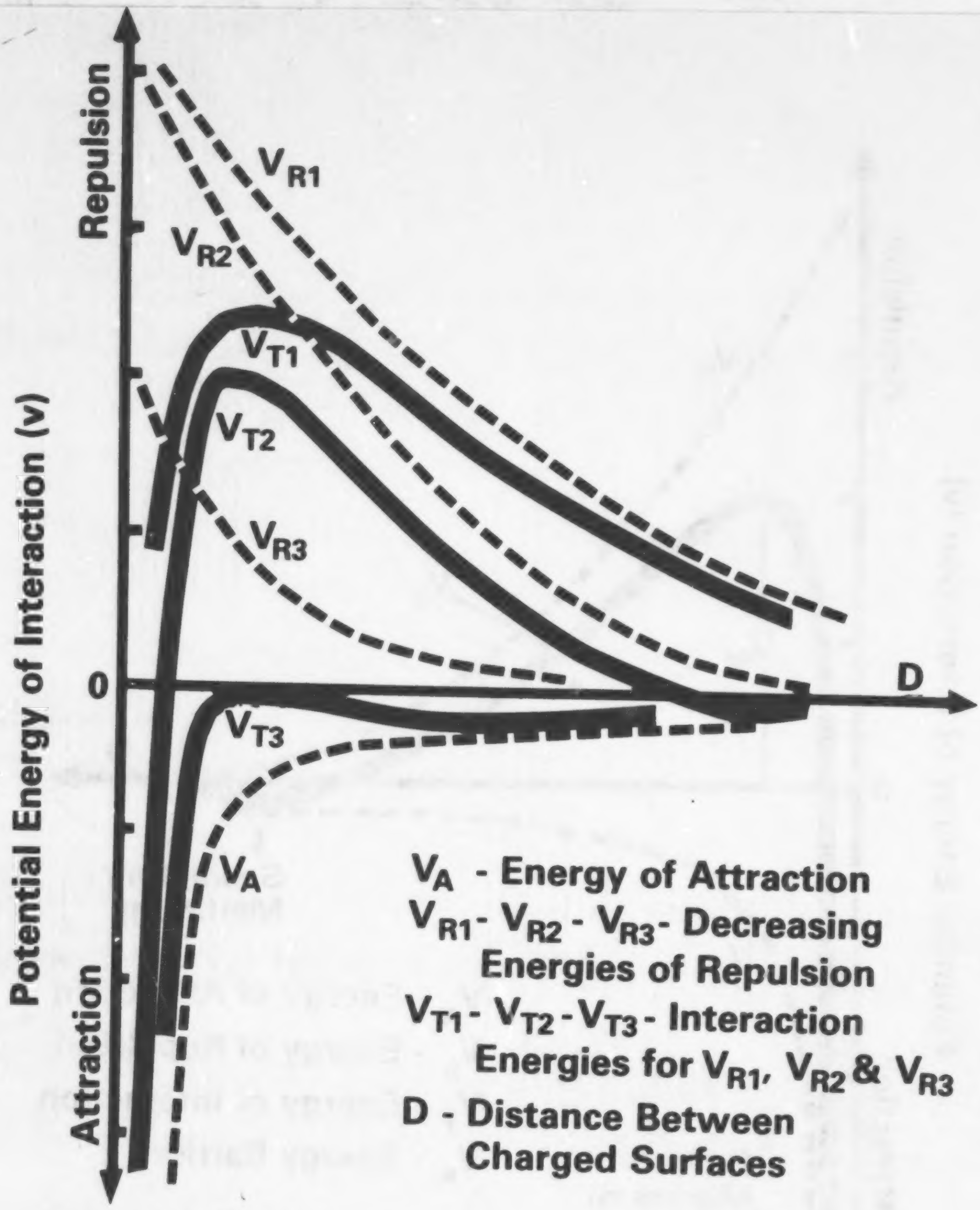


Fig. 19 Influence of Electrolytes on Interaction Energy

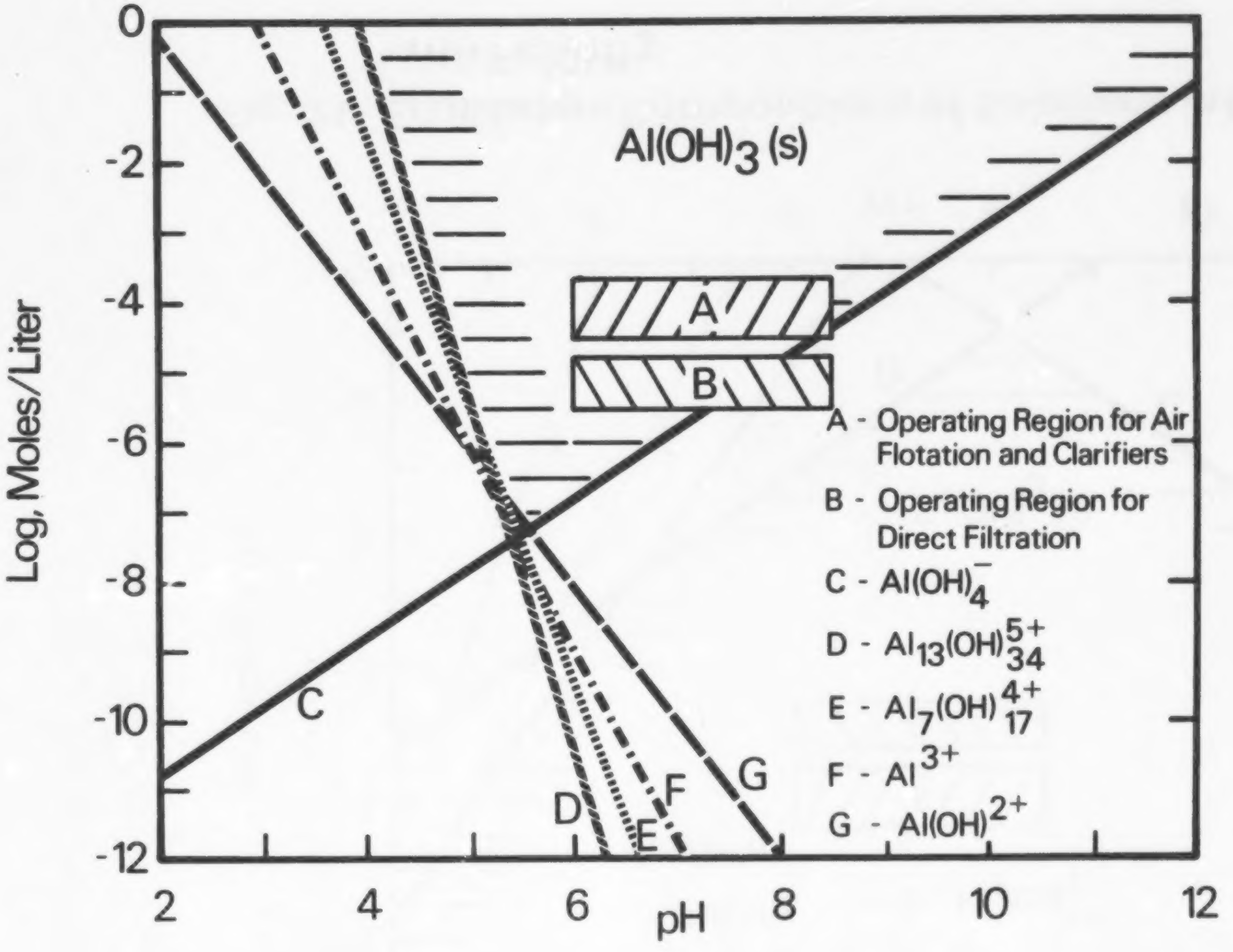


Fig. 20 Equilibrium Compositions of Solutions in Contact with $Al(OH)_3$

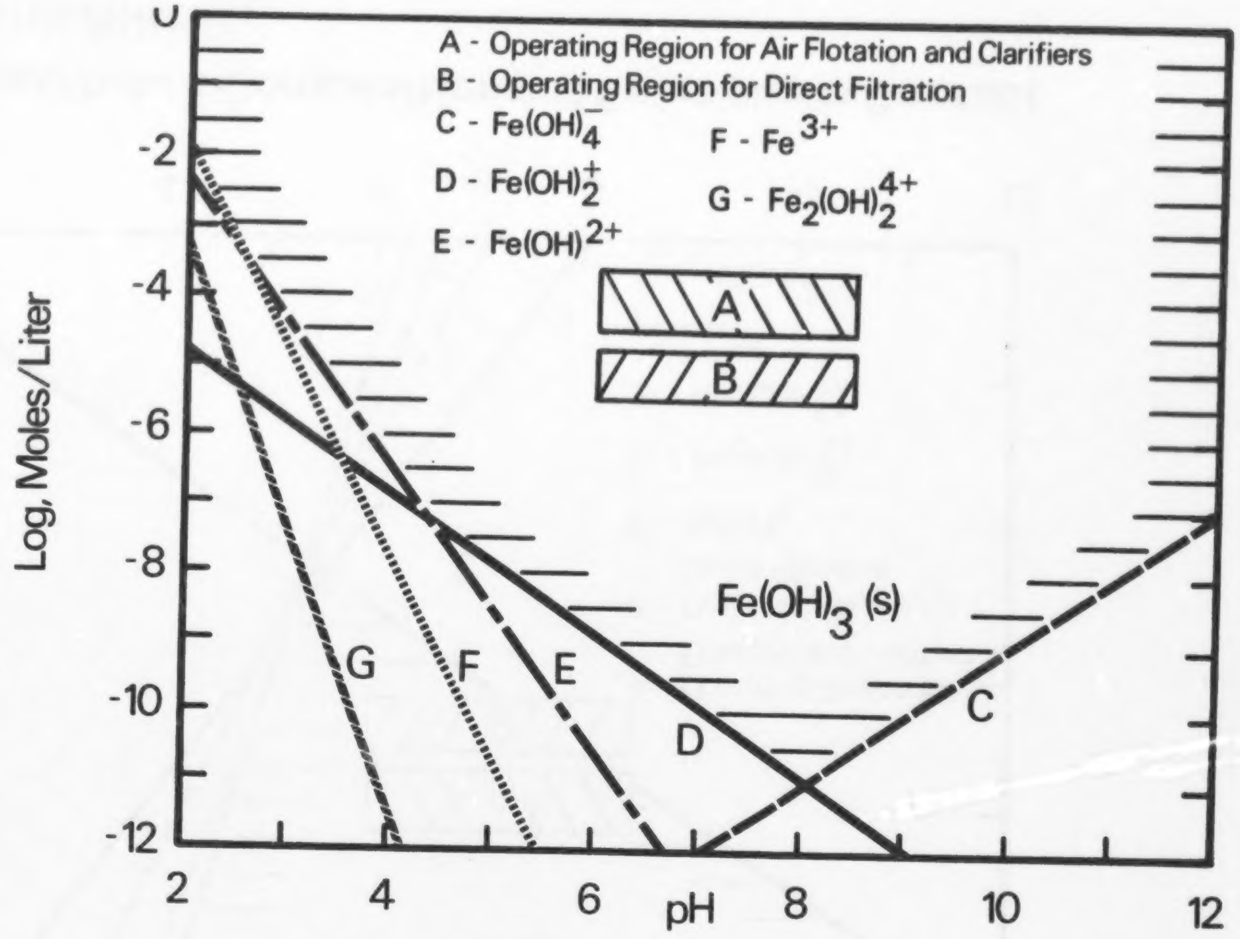


Fig. 21 **Equilibrium Compositions of Solutions in Contact with $Fe(OH)_3$**

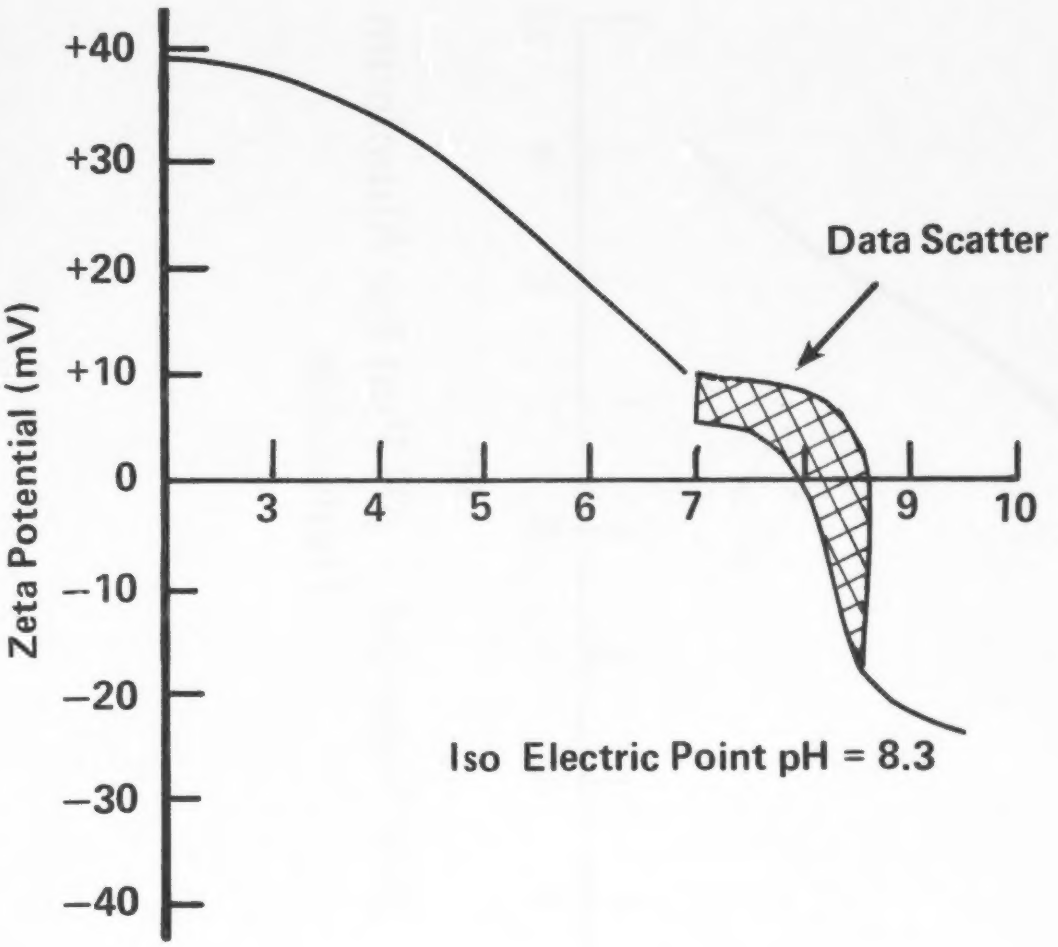


Fig. 22 Zeta Potential of Colloidal Iron Hydroxide Solutions Plotted As A Function of pH

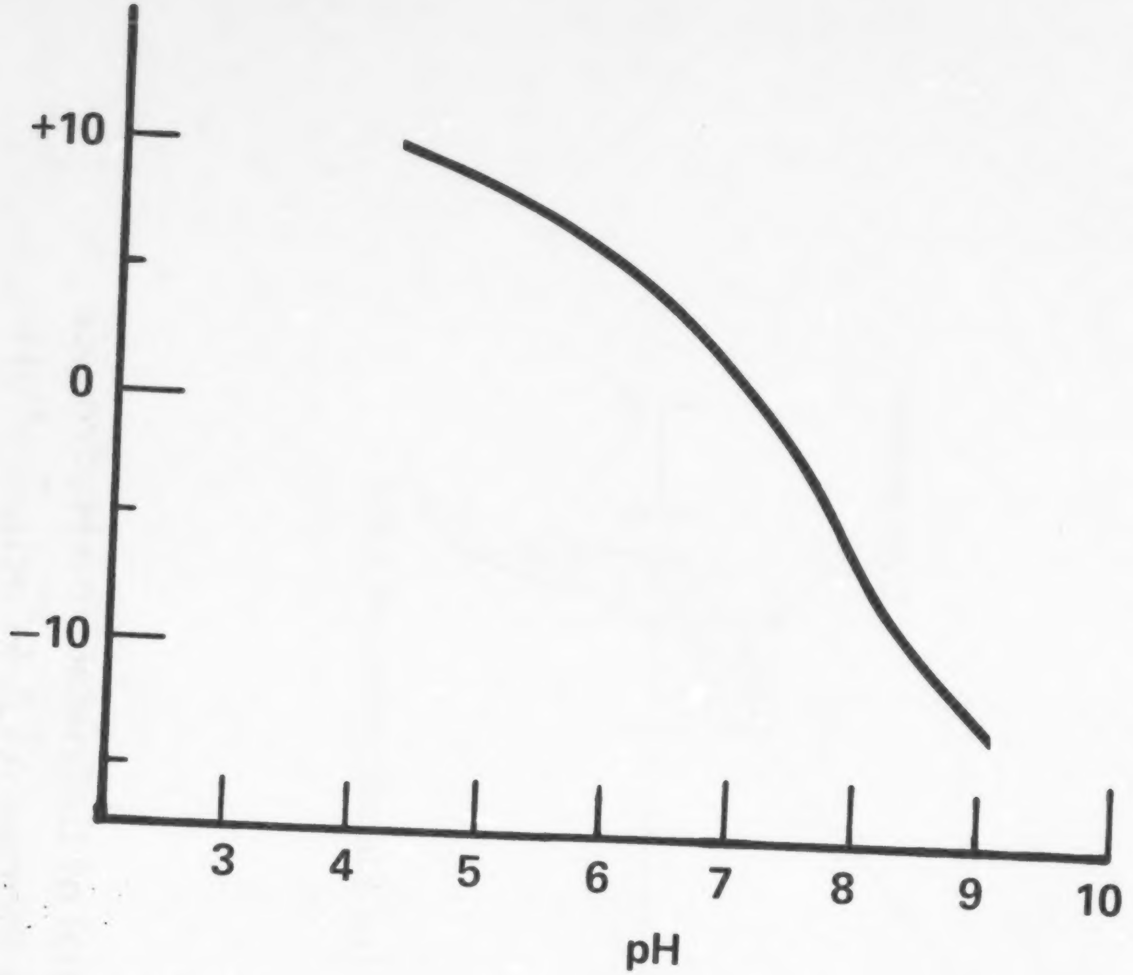


Fig. 23 Zeta Potential – pH Plot for Aluminum Hydroxide

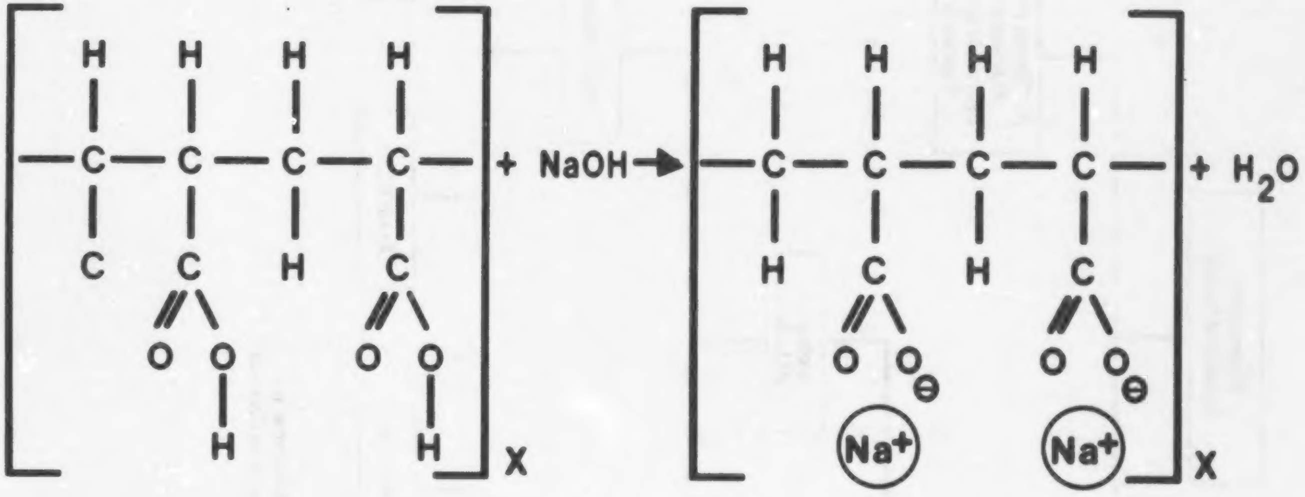


Fig. 24 Dissociation Of Polyacrylic Acid By NaOH

988

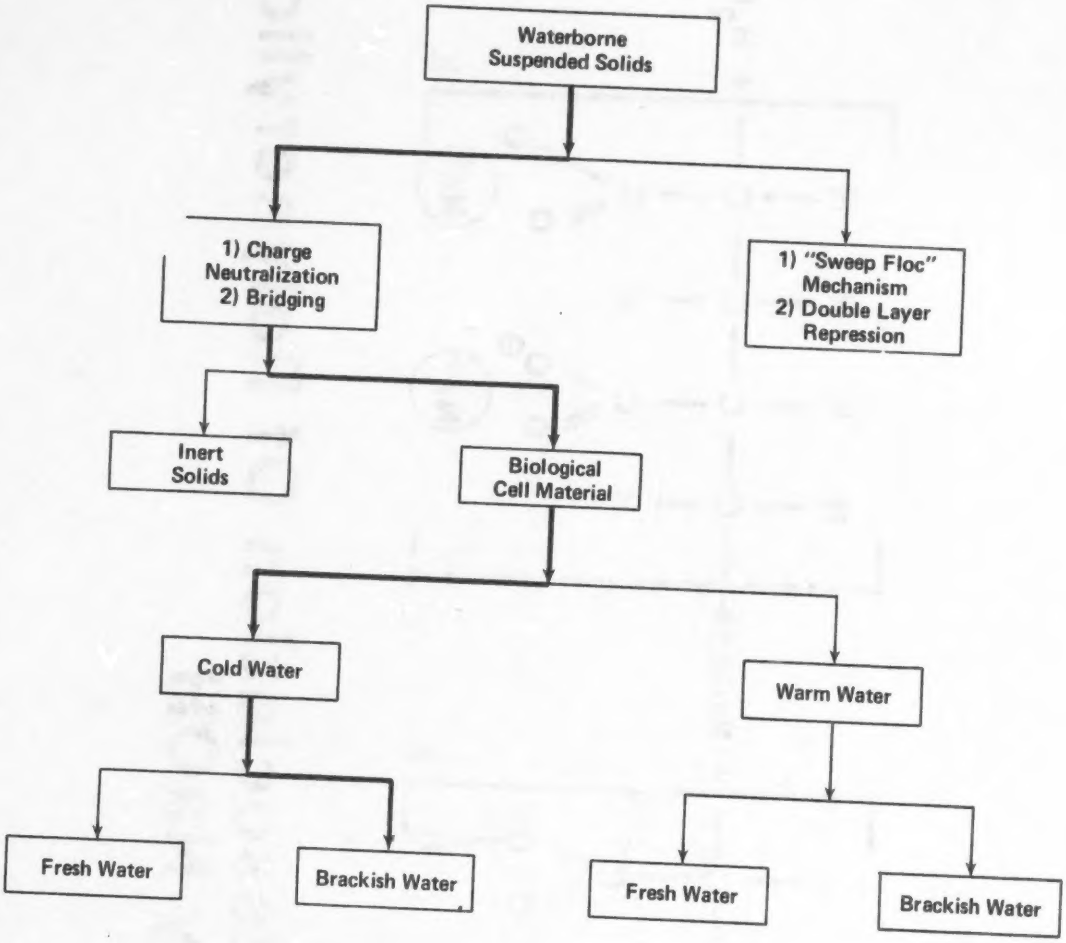
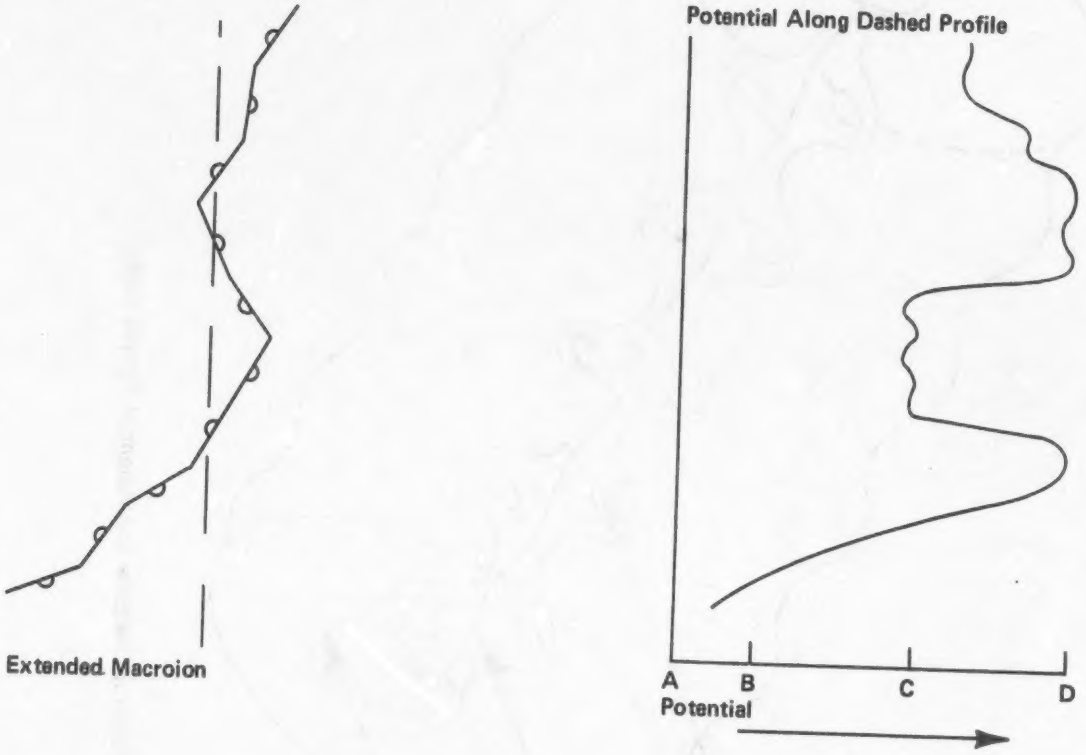

Waterborne Suspended Solids
1) Charge Neutralization 2) Bridging
1) "Sweep Floc" Mechanism 2) Double Layer Repression
Inert Solids
Biological Cell Material
Cold Water
Warm Water
Fresh Water
Brackish Water
Fresh Water
Brackish Water

Fig. 25 Condition–Response Flow Schematic for Chemical Treatment of Waterborne Colloids



A = Solution Potential; B = Weak Potential Field;
C = Potential Tunnel; and D = Potential Maxima

Fig. 26 An Extended Macroion and Its Associated Potential Field

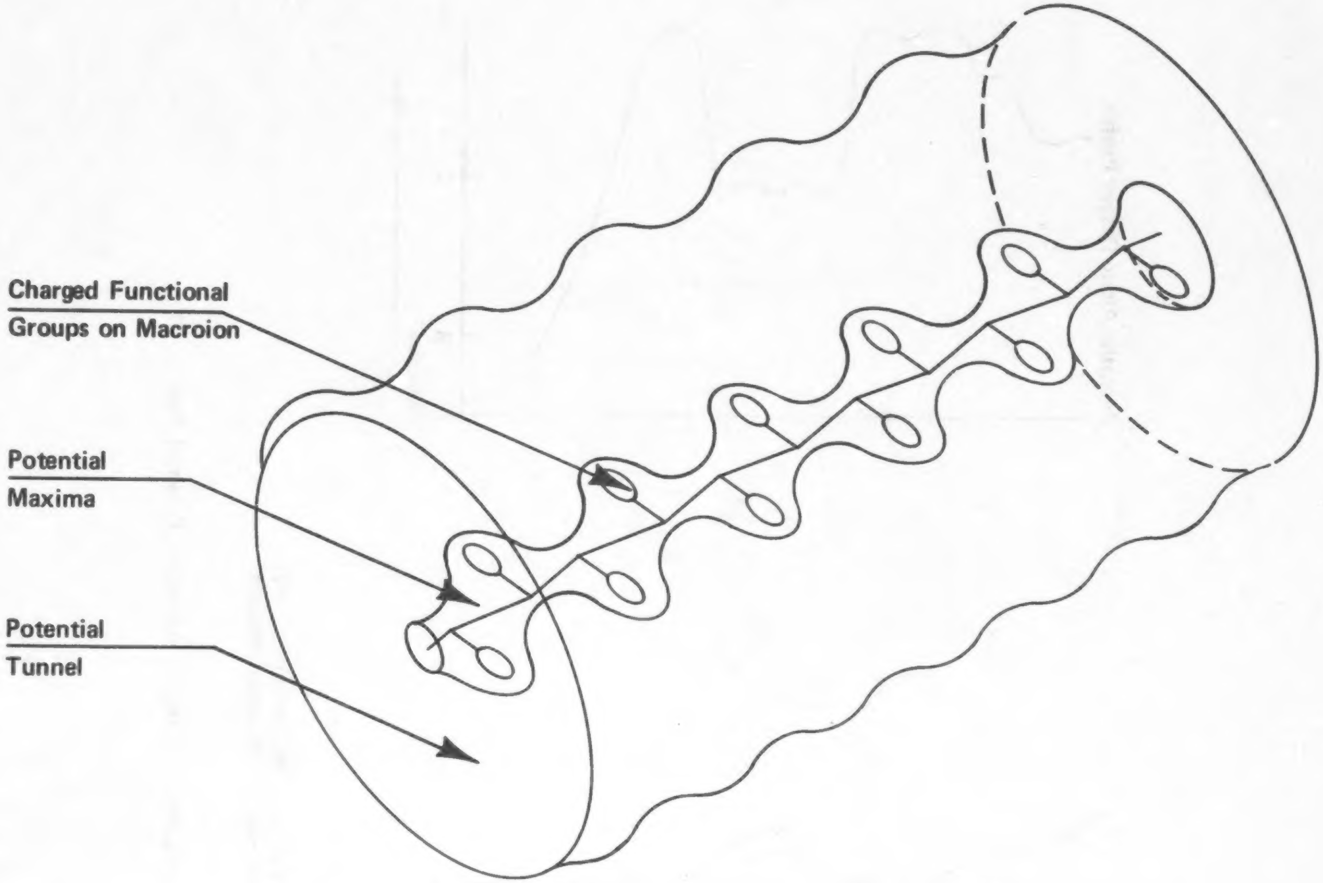
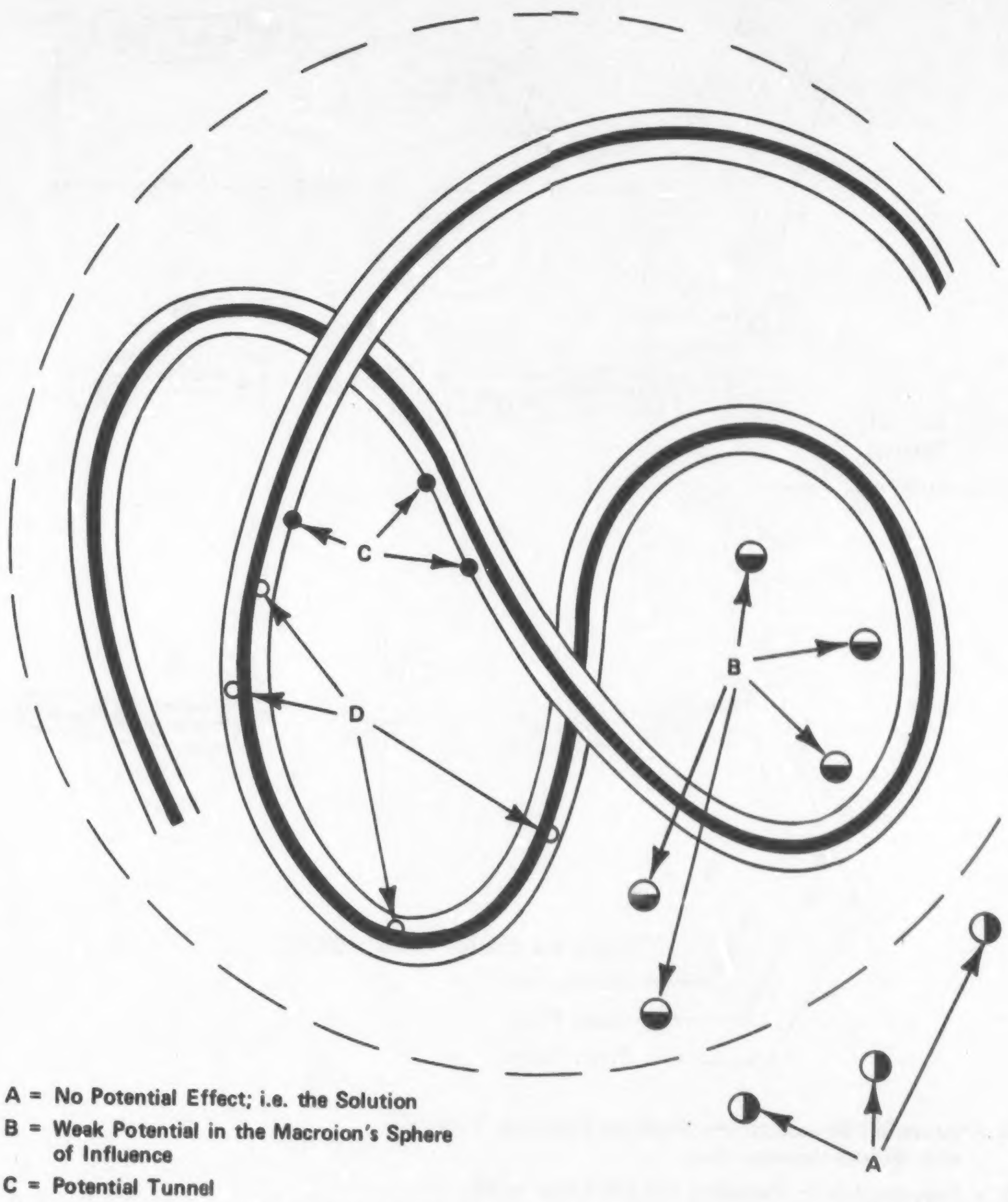


Fig. 27 Isometric Showing Potential Maxima and Potential Tunnel Fields



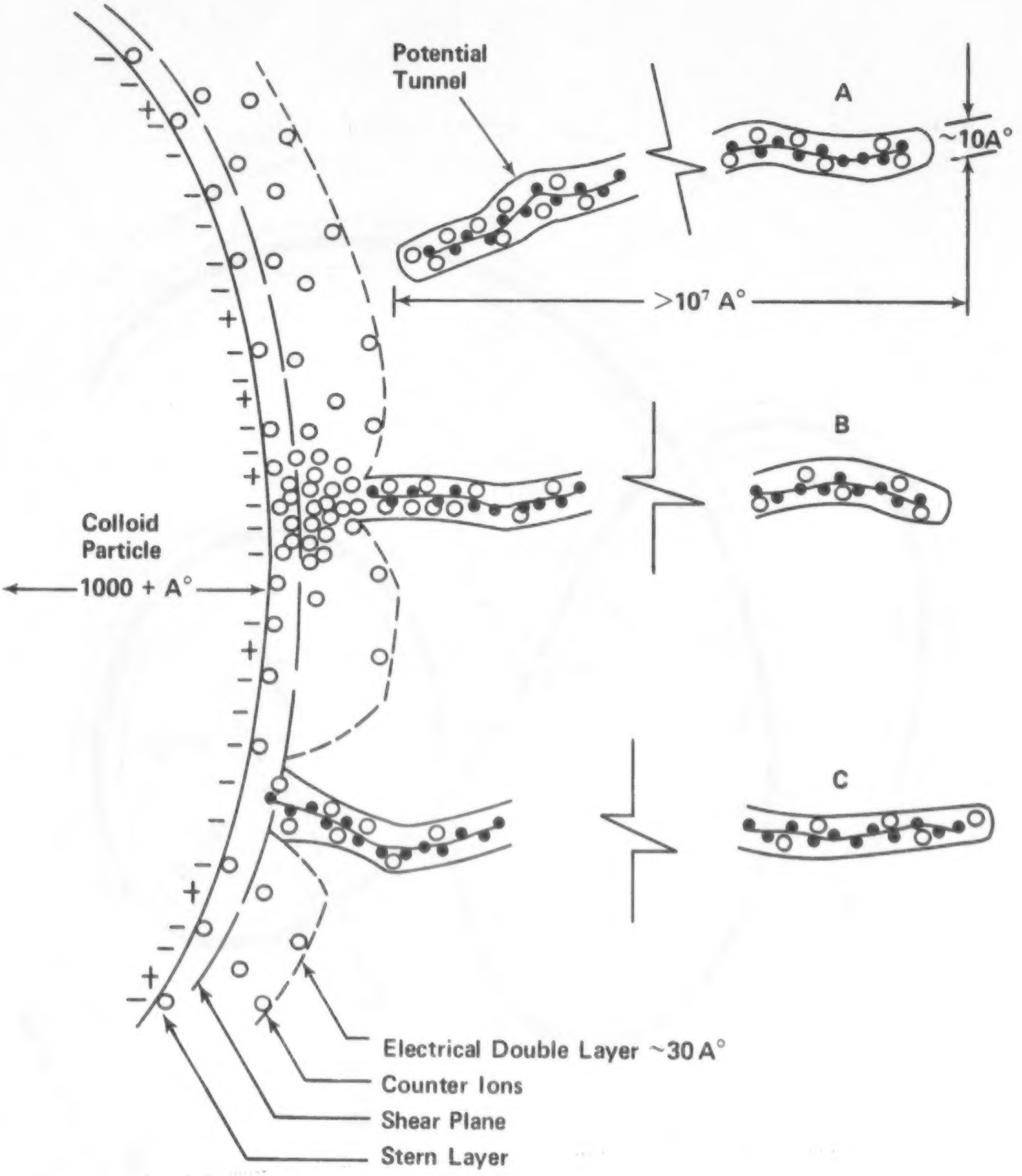
A = No Potential Effect; i.e. the Solution

B = Weak Potential in the Macroion's Sphere of Influence

C = Potential Tunnel

D = Potential Maxima Near Charged Functional Groups

Fig. 28 Macroion in Random Coil Conformation Showing Four Potential Regions

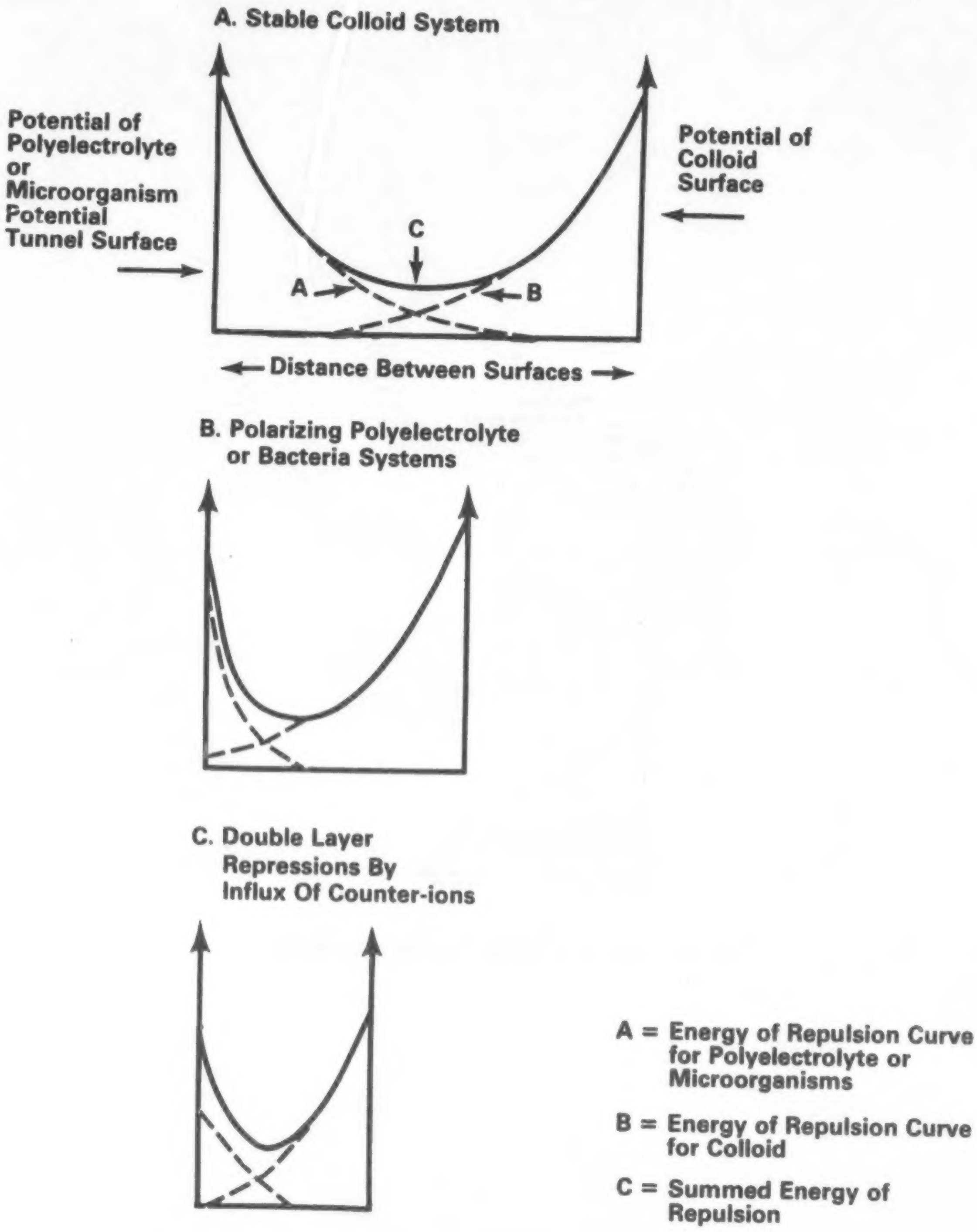


A = Anionic Polyelectrolyte Showing Potential Tunnel and Mobile Counter Ions

B = Polyelectrolyte Flooding Double Layer with Counter Ions

C = Chemically Bound Polyelectrolyte

Fig. 29 Electrical Model for Destabilization of Negative Colloid with Anionic Polyelectrolyte



A. Stable Colloid System

B. Polarizing Polyelectrolyte or Bacteria Systems

C. Double Layer Repressions By Influx Of Counter-ions

A = Energy of Repulsion Curve for Polyelectrolyte or Microorganisms

B = Energy of Repulsion Curve for Colloid

C = Summed Energy of Repulsion

Potential of Polyelectrolyte or Microorganism Potential Tunnel Surface
Potential of Colloid Surface
C
A
B
Distance Between Surfaces

Fig. 30 Polarization Affects Distance Between Surfaces

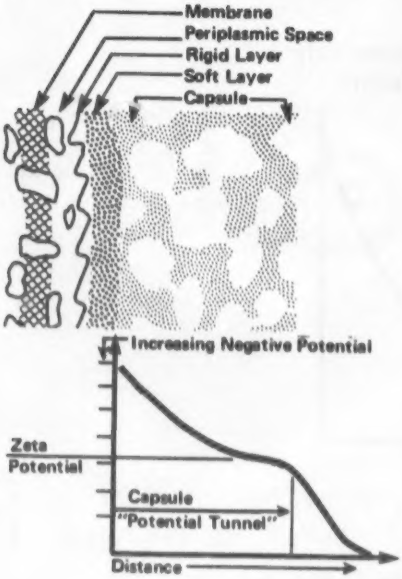


Fig. 31 Activated Sludge Floc Potential Model

"CONSIDERATIONS IN REUSE OF REFINERY WASTEWATER"

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ABSTRACT

Refineries typically recover all usable heat at process units; the waste heat dissipated by evaporative cooling towers and air coolers is of such low quality that recovery historically has been neither economic nor practicable. Refinery effluent water reuse, however, presents a unique opportunity for utilization of this waste heat for the reduction of wastewater volumes because the process technology used for evaporation can use this low grade waste heat as an energy source. Increasing present day and future energy costs increases the attractiveness of the approach for those situations where it is needed. Results from two successful experimental programs conducted as part of studies involving refinery wastewater reuse are discussed.

DISCUSSION

In 1973, NUS Corporation initiated a project for the API to develop methods of water reuse that could be employed to reduce wastewater flows from grass roots oil refineries. The studies were undertaken with the premise that all characteristic refinery water use practices and patterns would be considered so that comprehensive water management programs could be evolved. In essence, the multiplicity of refinery water and wastewater streams were viewed as parts of a single system. This approach permitted the development of bases for defining optimum approaches to water use and reuse.

The advantage of studying a hypothetical grass roots refinery was the freedom to employ any practical water use patterns and add treating equipment to alter water characteristics without the necessity of considering backfit penalties.

The model refinery was established with all of the normal unit operations of class D refineries including the following:

1. Atmospheric and vacuum distillation
2. Hydrocracking
3. FCC
4. Sulfuric acid alkylation
5. Catalytic reforming
6. Coking
7. Lube processing
8. Gas recovery
9. Gasoline sweetening
10. Desulfurization
11. Sulfur recovery
12. BTX
13. Gasoline blending

During the course of these studies, operating refineries for the most part already had BPT end-of-pipe treatment systems in place or under construction to meet the 1977 compliance date. This specific project was initiated looking ahead toward the probability of more stringent controls for 1983. It was recognized that additional processes to further reduce pollutants might be necessary and that treatment of large wastewater volumes would probably be exceedingly costly. On this basis effluent reduction could effect a dual benefit, i.e., the improvement in treatment efficiency of current systems and the reduction in future capital outlays and operating costs for 1983 BAT compliance.

The model refinery used for the studies had wastewater flows and qualities typical of a conventional 150,000 bbl/day class D refinery as a base case situation. The studies considered three different water supplies among many variables. Included was a low solids water typical of the Gulf Coast area, an intermediate solids water similar to Mississippi River water and a high bicarbonate alkalinity water similar to Lake Michigan.

A complete water balance was developed for each supply with resulting discharge volumes from 31 to 36 gallons per barrel of crude for the base conditions. In addition the following utilities requirements were assumed for the studies:

Steam Generation	20,000,000 lb/day
Cooling Load	50 x 10^9 BTU/day
Electrical Load	681,500 KW/hr/day

Pretreatment methodology and recycle schemes developed in the study showed that reduced effluent volumes of 7 to 11 gallons per barrel of crude were possible.

With this smaller volume of effluent as a basis for further investigations, two additional processes for further effluent reduction were applied. Both systems had the advantage of utilizing waste heat from the refinery.

The concepts employed to reduce flow from 7 to 11 gallons per barrel to lower values included a concentrating cooling tower and a brine concentrator as shown schematically in Figure 1. Figure 1 also shows a non-specific waste treatment plant upstream of the above referenced equipment. Determining the extent of waste treatment necessary in order to use wastewater as makeup to either or both systems was an important objective of the studies.

Concentrating Cooling Tower Tests

A cooling tower for concentrating wastewater could theoretically be used to reduce effluent volumes by evaporating water up to the solubility limit of the least soluble inorganic salt present. The concept was considered to be attractive since the capital cost of such a tower was considerably less per unit of water evaporated than other alternatives (such as a brine concentrator) and only slightly more expensive than normal cooling tower capacity. The cooling capacity of a concentrating tower would be substituted for other refinery cooling and the operating cost (electrical power required) would be essentially a trade-off.

In order to examine the feasibility of such a system a pilot plant was tested using refinery wastewater as makeup. During the operation of the pilot plant, scaling and corrosion data was of primary importance as was the fate of organics and other volatile compounds introduced in the makeup water.

The cooling tower selected for the tests was a coil shed type as depicted in Figure 2. It was in essence a normal induced draft tower with distributor nozzles in the bottom of an elevated collecting basin which distributed water to underlying cooling coils. The heat load to the tower was steam at 35 psig which admitted to the coils condensed and subcooled.

The pilot plant tests were conducted at a refinery. Extensive analyses of the wastewater to be used as makeup were conducted. Inorganic analyses focused on the phosphate, carbonate, sulfate, silica content which with calcium could form scale. Suspended solids was also considered as a possible depositing material. It was determined from the analyses that phosphate and silica would not be significant scaling materials and that calcium carbonate scale could be avoided by careful pH control using acid. It was simultaneously determined that calcium sulfate and suspended solids would be the likely potential sources of deposits.

During test runs suspended solids were concentrated to values exceeding 500 ppm in the tower without deposition. This left the deposition of calcium sulfate of primary concern.

Figure 3 shows the solubility limit of calcium sulfate as a function of temperature. During tests, the bulk water temperature was 105°F as indicated by Point No. 1. This according to literature should have been the maximum concentration of calcium sulfate attainable without scaling. Point No. 2 corresponds to a skin temperature of 200°F. Point No. 3 indicates the solubility limit at the skin temperature of the coil inlet equal to a 285°F steam temperature. Scaling actually occurred at Point No. 4 conditions as a result of the film boiling. Scaling started at the steam inlet to the coil and progressed across the first tubes.

Although the coil shed tower was selected primarily for accessibility of the heat exchangers, the direct cooling of process fluids in the tower limits the usefulness of the concept and an intermediate cooling loop to eliminate the occurrence of film boiling as well as to reduce skin temperature is required to achieve higher concentrations of dissolved salts and thereby extend the usefulness of the concept.

Figure 4 shows by arrows the conditions in the test program where crystalline deposits developed. It was determined that a short chain polyacrylate with acid pH control utilizing hydrochloric for Test 7 and sulfuric for Tests 9 and 10 was effective in suppressing crystalline deposit formation on the tubes. It was therefore concluded that these materials would be very effective in assuring reliable operation of a system where calcium sulfate was controlling. With proper design, system pH control and with the short chain polyacrylate as an additive, it is realistic to conclude that calcium sulfate concentrations of 2500 ppm could have been tolerated without crystalline deposit formation. During Tests 7, 9 and 10, only a light powdery film developed in insufficient quantities to sample. The material could be removed easily by water sprays.

The full test program encompassed evaluations of the following chemical control conditions:

1. No chemical addition
2. Sulfuric acid for pH control, pH 7.1-7.2
3. Repeat of No. 2, pH 6.8-7.1
4. Organic phosphate (100 ppm), sulfuric acid, pH below 8.0
5. Organic phosphate - polyacrylate (100 ppm)
6. Combination short & long chain polyacrylate (100 ppm) with sulfuric acid pH control
7. Short chain polyacrylate (100 ppm), HCl pH control
8. HCl alone, pH 6.9-7.1
9. Short chain polyacrylate, repeat of Test No. 7, with sulfuric acid
10. Short chain polyacrylate, repeat of Test No. 9

During pilot plant operation, data was collected to determine the fate of the organics present in makeup water. Test data is included in Table 1. The concentration of both the phenols and ammonia in the recycle water were lower than those in the makeup water.

Data was collected under both sterile and unsterilized conditions with the same results. The reduction in total carbon, ammonia and phenols was therefore attributed to air stripping in the tower and not due to biological oxidation. Consequently, it was further concluded that thorough and effective treatment of refinery wastewater makeup is necessary to prevent air emissions due to stripping. Conventional wastewater treatment with oil separation, equalization, air flotation or filtration, biological oxidation and final solids removal would be desirable.

Brine Concentrator Tests

A survey of refinery wastewater conditions indicated that a brine concentrator could be economically employed for effluent reduction if the stream to be treated was of low volume and if the device would operate successfully on refinery wastewater without scaling and produce water of condensate quality which could be used as a substitute for boiler makeup water. A small pilot evaporator using the calcium sulfate seed slurry scale control process was operated on a Texas refinery wastewater. A series of four tests were conducted during which the volume of evaporator blowdown was successfully reduced to 1% of the evaporator makeup water. Soluble salt concentrations in recirculating brine reached 300,000 ppm and suspended solids reached 80,000 ppm during the tests without deposition on the heat transfer surfaces.

Oil in the makeup water to the evaporator ranged from 1 to 3 ppm but caused no problem.

No corrosion of the 316 stainless steel evaporator occurred except during an early run when the feedwater was poorly deaerated which in conjunction with iron concentrations of approximately 30 ppm led to slight pitting of the stainless steel heat transfer surfaces.

The distillate water produced by the brine concentrator contained 60% to 70% of the phenolic materials, 25% of the freon soluble oils, 25% to 50% of the ammonia and 50% to 60% of the total organic carbon introduced in the feedwater. It was therefore concluded that if the distillate was to be employed as boiler feedwater, conventional wastewater treatment processes would be required upstream of the evaporator.

In summary, it was determined that with the refinery wastewaters tested, both the concentrating cooling tower and brine concentrator are viable methods for reducing wastewater flow.

The concentrating cooling tower enjoys the universal advantage of utilizing waste heat normally rejected in conventional cooling towers. The brine concentrator finds its most economical application in plants where low pressure steam that would otherwise be vented is available as an energy source. However, in some situations where the value of the recovered water for boiler use is great enough based upon alternative raw water treatment costs, operation on the vapor compression cycle using electric energy input may be justified.

BIOGRAPHY Paul Goldstein

Paul Goldstein is Vice President and General Manager of the Cyrus Wm. Rice Division of NUS Corporation. He holds a B.S. degree in Marine Engineering from the United States Merchant Marine Academy. Prior experience includes techanical management with Combustion Engineering, Inc. and Senior Research Engineer with Foster Wheeler Corporation.

Robert W. Griffin received a B.S. degree in Chemical Engineering from Grove City College. He is currently Manager of Special Projects fro NUS Corporation, Pittsburgh, Pennsylvania. He has been with NUS Corporation since graduation in 1950. Mr. Griffin is also a Consulting Engineer.

PAPER DISCUSSION

Question - Bill Ruggles, Phillips Petroleum Company

What corrosion rates were observed during use of highly concentrated wastewater during cooling tower tests?

Answer

Each test conducted was of short duration making it impractical to collect meaningful corrosion data. We were concentrating on the scaling data and once the tubes were scaled it was necessary to lower pH dramatically to remove the deposit. The coil was made with four passes and the tubes were two rows of stainless, one row each of Admiralty and 90-10 cupro-nickel. After the test runs there was no evidence of corrosion on the tubes either generalized or pitting. We would expect corrosion rates on carbon steel to be similar to those experienced on brackish waters where somewhat higher inhibitor concentrations are required.

Question - Jeffrey Chen, Dravo Corporation

What do you do with the concentrated brine?

Answer

There is no specific answer to the problem of brine disposal, however, it is somewhat site specific. The brine concentrator decreased effluent volume to one or two gallons of water per barrel of crude processed. It could be decreased further by a drier. Of the total dry salt produced over 50% came from ballast water (150,000 gal/day) which was included in the study and represented a salt on a dry basis of 15 to 20 tons per day. Answers to the question depending on the location could be deep well disposal, ocean disposal, on-land in arid regions or possibly reprocessing.

TABLE 1

ANALYSES DURING TEST RUN

Date	Makeup Water	Recycle Water	Calculated From Cycles
CARBON			
2/6	92	185	506
2/17	79	374	671.5
2/20	81	458	753.3
2/26	69	278	607.5
3/1	60	326	531.1
3/5	74	461	488.4
3/10	69	323	828
3/19	60	380	834
3/26	68	300	595
AMMONIA			
2/6	3.7	4.8	20.35
2/17	5.4	13.0	45.9
2/20	6.1	0.84	56.73
2/26	8.0	1.3	45.75
3/1	1.9	0.4	14.63
3/5	-	0.82	-
3/10	2.6	3.0	31.2
3/19	3.2	1.2	44.5
3/26	3.3	2.9	28.9
PHENOLS			
2/6	0.2	0.1	1.1
2/17	0.26	0.25	2.21
2/20	0.20	0.26	1.86
2/26	0.254	0.092	1.5
3/1	-	0.229	-
3/5	0.299	0.239	1.97
3/10	-	0.02	-
3/19	0.330	0.286	4.59
3/26	0.495	0.411	4.33

FIGURE I
PROPOSED EQUIPMENT USE

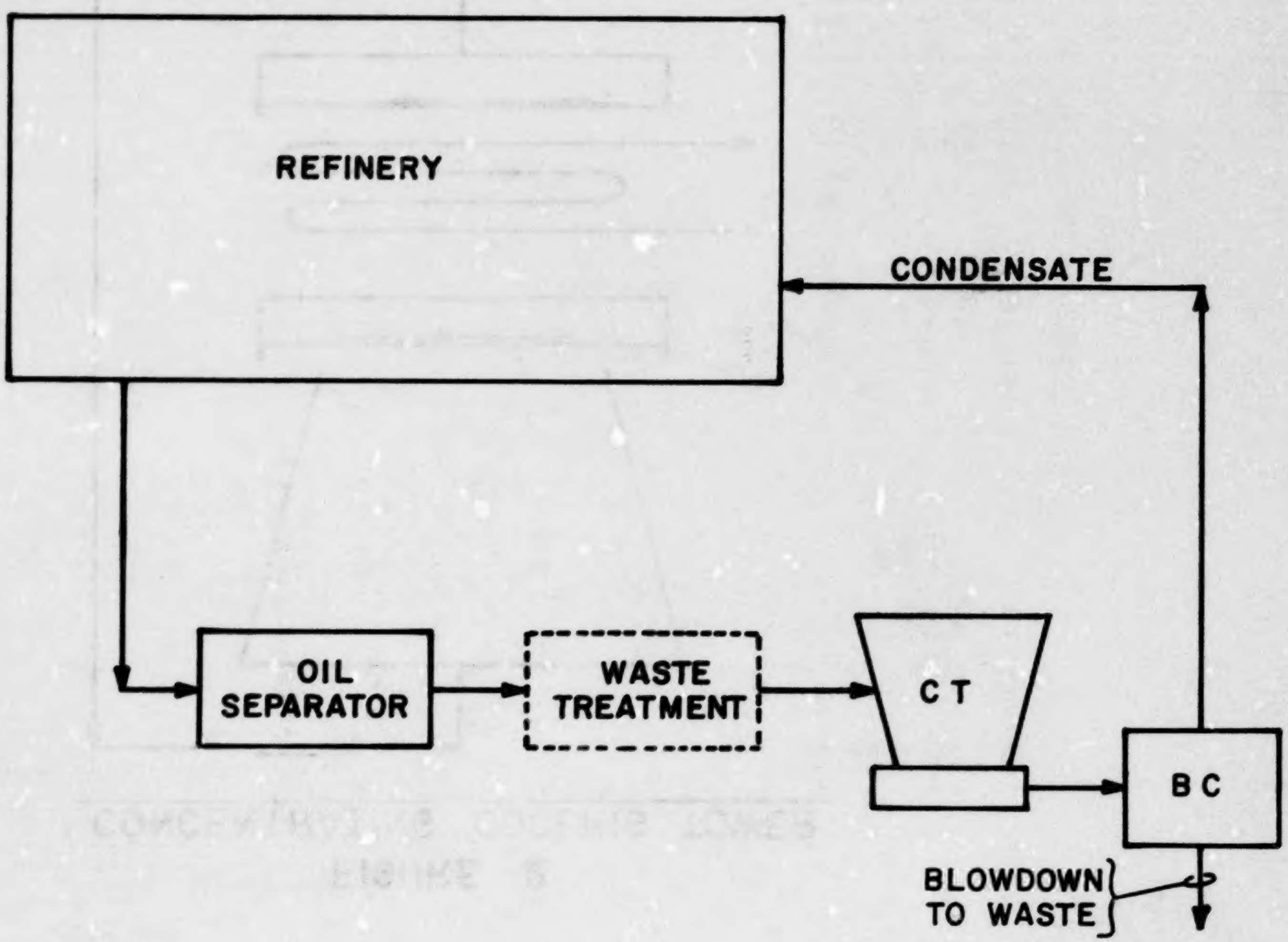


FIGURE 2
CONCENTRATING COOLING TOWER

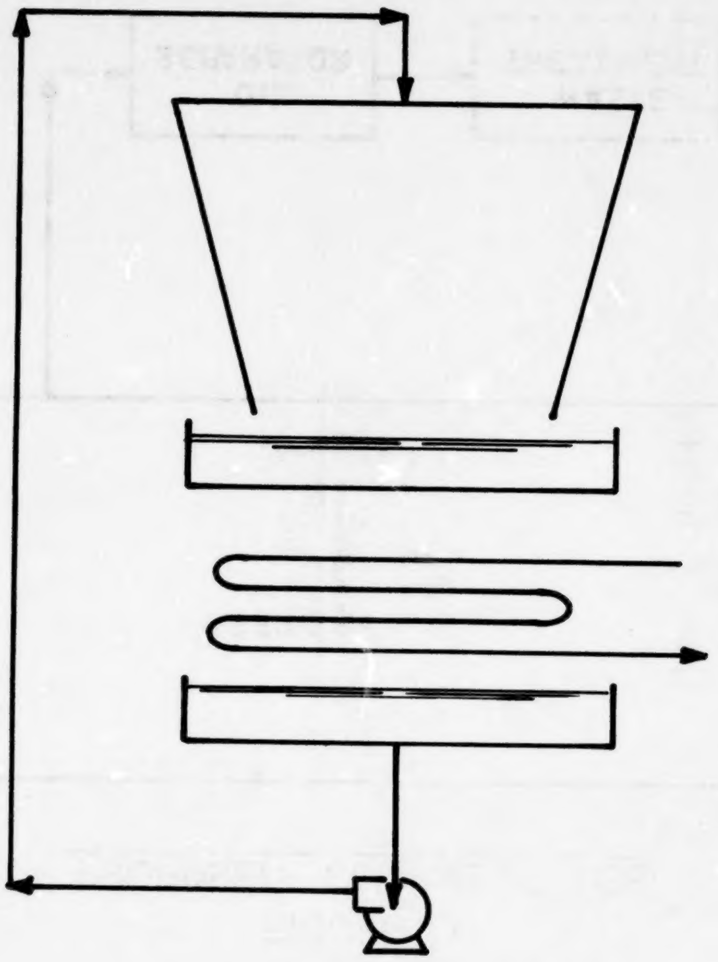


FIGURE 3

THEORETICAL AND ACTUAL
CALCIUM SULFATE SOLUBILITY VS. TEMPERATURE
FOR CONCENTRATING COOLING TOWER DEMONSTRATION

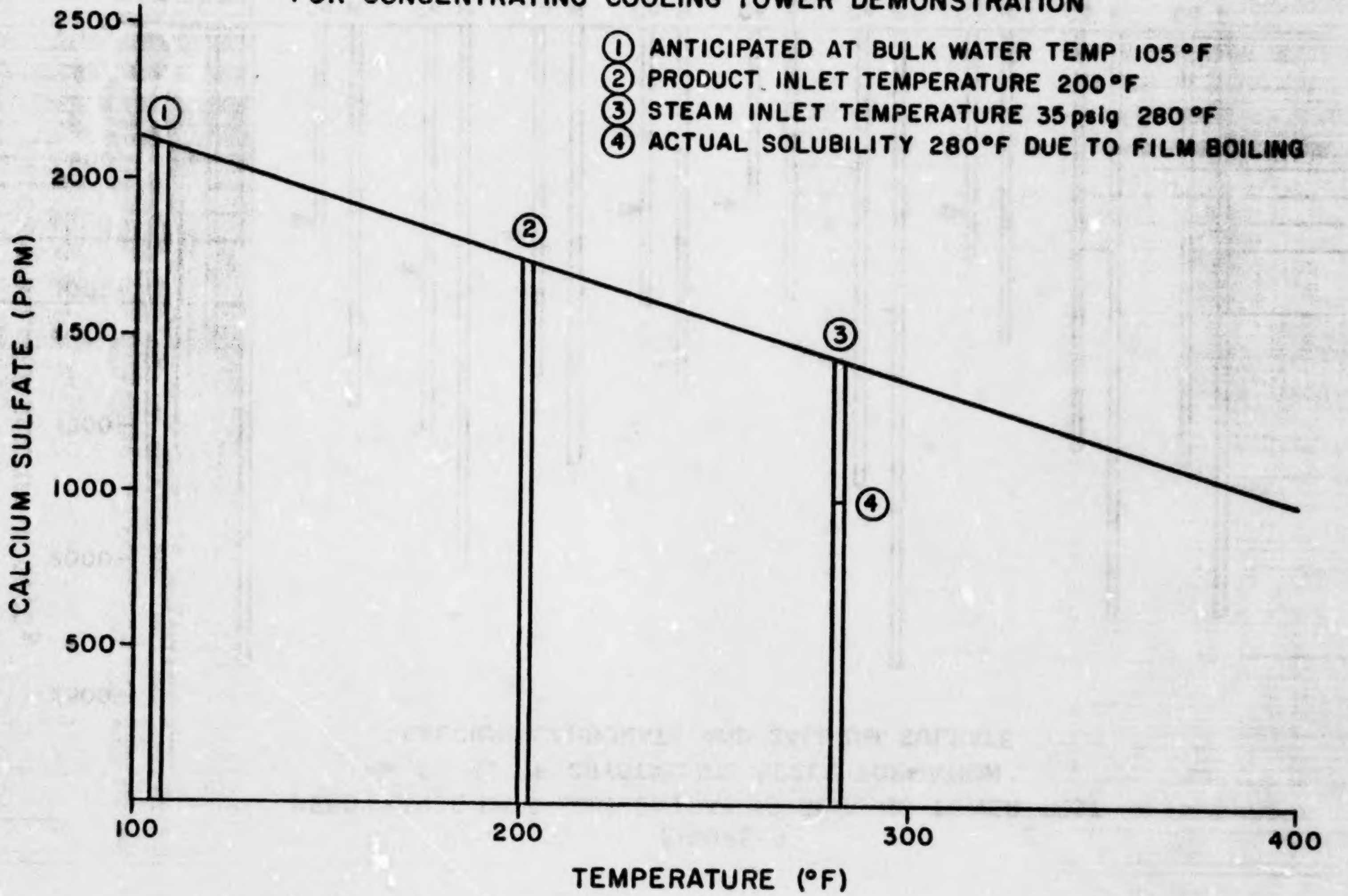
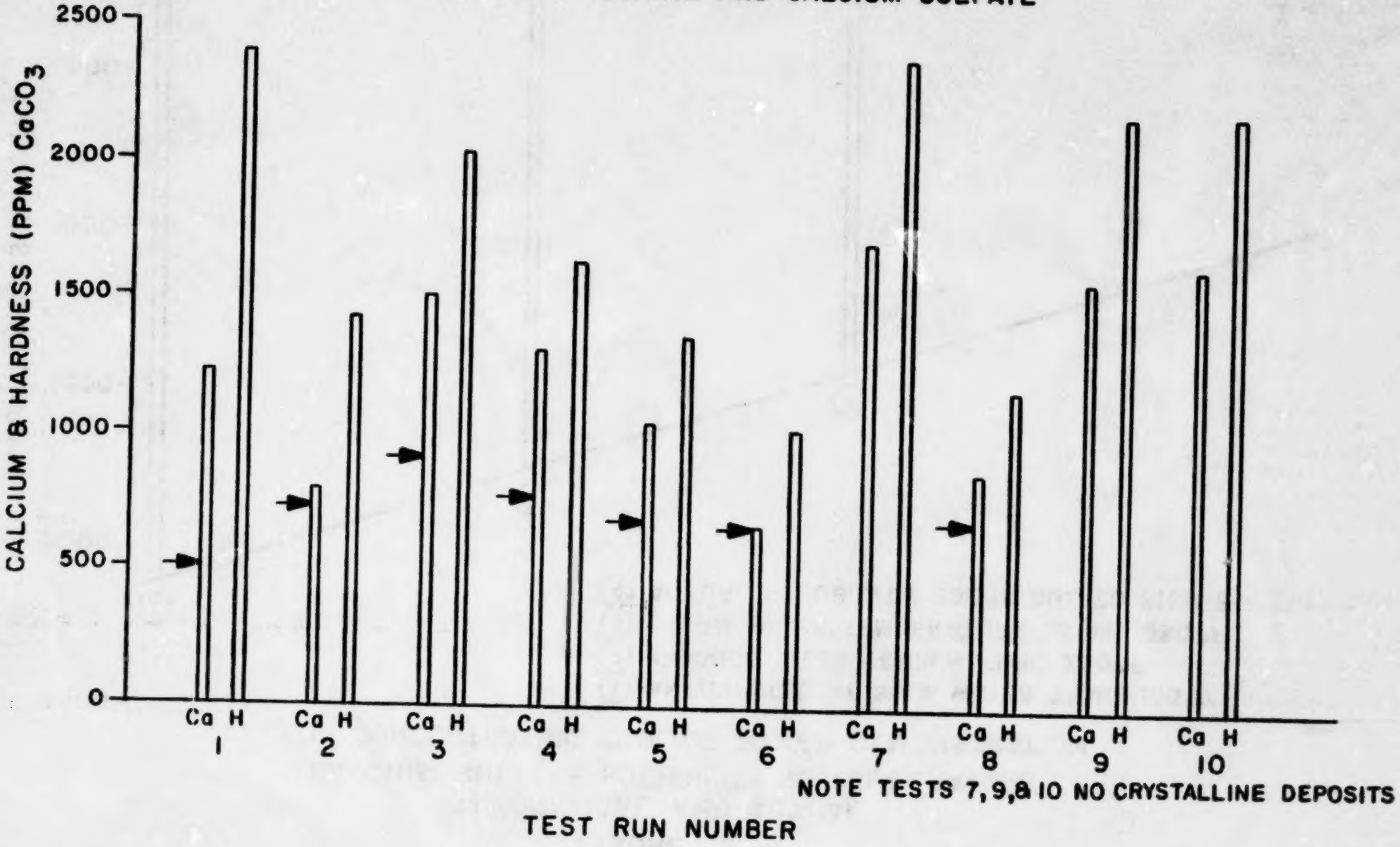


FIGURE 4

PERORMANCE DATA CONCENTRATING COOLING TOWER TEST

→ POINT OF CRYSTALLINE SCALE FORMATION

CALCIUM CARBONATE AND CALCIUM SULFATE



NOTE TESTS 7, 9, & 10 NO CRYSTALLINE DEPOSITS

STATE-OF-THE-ART IN SOUR WATER STRIPPING

M. R. Beychok
Consulting Engineer

Sour water effluents from refining and petrochemical plants originate primarily from the use and subsequent condensation of process steam. The condensation usually occurs in the presence of a hydrocarbon vapor phase containing various amounts of NH_3 and H_2S. Thus the condensed steam often contains NH_3 and H_2S in amounts ranging from 1,000 to 10,000 ppm which imparts the unpleasant odor characteristic of sour waters. Some sour waters, particularly from hydrocrackers, may contain as much as 30,000 to 50,000 ppm of NH_3 and H_2S.

Sour waters may also contain significant amounts of CO_2, phenols, cyanides, fatty acids and other contaminants. Fortunately, the principal contaminants, NH_3 and H_2S, can be removed by relatively simple steam distillation (stripping). Traditionally, the refining and petrochemical industries have stripped NH_3 and H_2S from their sour waters by steam distillation at 5-10 psig and 230-240 °F. The stripping steam is either injected directly into the distillation tower or generated in reboilers.

A systematic study of sour waters and a tray-by-tray design method for sour water strippers was first published in 1967(1). At that time, the typical refinery sour water stripper involved:

- About 8-10 trays
- A stripping steam rate of about 0.8 pounds of steam per gallon of raw feed (lbs/gal RF)
- 69 % (or more) average NH_3 removal
- 95 % (or more) average H_2S removal
- Tray efficiencies of about 40-50 %

In 1972, the American Petroleum Institute (API) undertook a detailed survey of sour water strippers(2). The results of that survey are summarized in Table 1 herein. Briefly, the 1972 survey indicated that the average sour water stripper involved:

- 15 trays
- A stripping steam rate of about 0.8 lbs/gal RF
- 78 % NH_3 removal
- 96 % H_2S removal
- Tray efficiencies of about 45 %

Clearly, very little had changed in the design or performance of sour water strippers between 1967 and 1972 other than a trend toward using more trays (15 rather than 10, as an average).

CURRENT DESIGN REQUIREMENT

In recent years, a number of 25 to 30 tray sour water strippers have been built. This trend toward a dramatic increase in trays has been necessitated by ever more stringent environmental regulations on the NH_3 content of discharged effluent waters. Whereas the traditional designs of sour water strippers had emphasized H_2S removals, environmental regulations now make it necessary that strippers be designed primarily for NH_3 removal.

As an order of magnitude, Table 2 illustrates that a typical 125,000 BSD refinery (within the EPA's cracking category) may require sour water stripping down to a level of 25-60 ppm of NH_3 to meet the EPA's refinery effluent guidelines for Best Available Technology Economically Achievable (BATEA). That level of 25-60 ppm of NH_3 in the stripped water is based on these criteria:

- -- The BATEA 30-day average guidelines for BOD and NH_3 translated to annual averages using the EPA's variability factors for BOD and NH_3
- -- Assuming the 125,000 BSD cracking refinery has a sour water rate of 300-350 gpm
- -- Assuming that 50-100 % of the BOD is removed in a biotreater (operating at 90 % efficiency) which consumes 4 pounds of Nitrogen per 100 pounds of BOD removed
- -- Assuming that 70 % of the nitrogen entering the biotreater comes from stripped sour water

Given a sour water containing 7,500 ppm of NH_3, it will require 99.2 to 99.7 % NH_3 removal to achieve a stripped water NH_3 level of 25-60 ppm. Regardless of the precise accuracy of the illustrative case in Table 2, it is fairly obvious that the current design requirement for NH_3 removal in sour water strippers should be at least 99 % and perhaps in excess of 99.5 %. Achieving such NH_3 removals requires more trays and/or steam as compared to the average stripper in the 1972 API survey. In the current era of high fuel costs and emphasis on energy conservation, it is important that the design engineer carefully evaluate the tradeoff between trays and stripping steam in achieving a desired NH_3 removal. Figure 1 is from a recent publication(3) of a stripper design study, and it illustrates the tradeoff between incremental trays and incremental stripping steam. It shows that 99.4 % NH_3 removal could be achieved, for the specific study, by either of the combinations of equilibrium stages and stripping steam listed below (from which we can obtain the tradeoff between incremental trays and incremental steam):

Stages		Stripping Steam	
Equilibrium	Actual	lbs/gal RF	lbs/gal TF
9.3	21	1.1	1.0
6.0	13	1.8	1.5

Thus an increment of 8 actual trays could replace an increment of 0.7 lbs of steam/gal RF. For a stripper raw feed rate of 350 gpm, that amounts to 353,000 lbs/day of steam savings as the tradeoff against using 8 more trays. The savings are in fact even larger since the higher steam rate would increase the size of the stripper tower, reboiler and overhead condenser. In this specific case, it is obvious that the correct design choice would be to use more trays rather than more stripping steam.

RECENT AND ONGOING RESEARCH ON SOUR WATERS

After completing the stripper survey in 1972, the API retained the Bechtel Corporation to:

- Determine if phenols or cyanides affected the stripping of synthetic sour waters in a bench-scale stripper
- Determine if actual refinery sour waters stripped in the same manner as did synthetic sour waters
- Evaluate the validity of Van Krevelen's vapor-liquid equilibrium (VLE) data for the NH_3-H_2S-H_2O system

The results of Bechtel's work have been published by the API(4) and summarized in an excellent paper by Gantz(5). Briefly, Bechtel found that:

- -- Fresh synthetic solutions of NH_3 and H_2S, as well as actual refinery sour waters, both exhibited rapid and pronounced oxidation. This resulted in a "fixed" amount of NH_3 residual in stripped waters which could not be removed by intense stripping or batch boiling. Similar results had been reported earlier by Dobrzanski and Thompson(6).
- -- Fresh synthetic solutions of NH_3 and H_2S (protected from oxidation) could readily be stripped to very low levels of both components. Levels of 10-15 ppm NH_3 and 0-5 ppm H_2S were achieved with 5-10 bench-scale trays and stripping rates of 1.0-1.8 lbs/gal RF. (The 5-10 bench-scale trays were probably equivalent to 10-20 plant scale trays).
- -- The addition of as much as 800 ppm phenols and 120 ppm cyanide did not affect the ability to strip NH_3 and H_2S from the fresh synthetic sour waters.
- -- Actual refinery sour waters all contained a varying amount of "fixed" residual NH_3 after stripping which was attributed to either oxidation or some unknown acidic compounds present in the sour waters.
- -- Caustic injection into the stripper could be used quite effectively to release the "fixed" NH_3 and to achieve

low levels of NH_3 in stripped waters.

-- The Van Krevelen VLE data were valid for synthetic and actual refinery sour waters, if proper allowance was made for any "fixed" NH_3 residual as determined by a batch boiling test.

Following Bechtel's work, the API and the EPA jointly funded Stanford Research Institute (SRI) during 1976-1977 to:

- Determine what acidic material were present in sour water and if there were other causes for NH_3 fixation.
- Study caustic injection strategies.
- Determine the behavior of cyanides during stripping.

The results of SRI's work have been described by Bomberger and Smith(7). A final report for publication is in preparation. Briefly, SRI found that:

-- There were numerous problems associated with the standard analytical procedures when applied to sour waters. In particular, the NH_3 determination procedures need much further developmental work.

-- The analytical procedures for cyanide were inadequate and the cyanide stripping studies were therefore not concluded.

-- Heavy metal contents were so low in the stripped waters that ammonia-metal complexes were eliminated as a cause of NH_3 fixation.

-- Most of the refinery sour water samples had significant amounts of oxidized sulfur compounds, and the oxidation had occurred in the refineries.

-- 12-40 % of the organics in the refinery sour waters were phenol and cresols.

-- NH_3 fixation was caused by weak sulfidic acids, weak organic acids and strong sulfidic acids:

Refinery	Weak acids (meq/l)	Strong acids (meq/l)	Total acid (meq/l)	Fixed NH_3 (meq/l)
B	<2.0	---	2.0	1.0
C	<2.0	4.8	6.8	11.0
D	2.9	0.5	3.4	2.1
F	3.9	1.0	4.9	6.2
G	<2.0	---	2.0	2.1
H	<2.0	3.4	5.4	4.2

-- The optimum caustic injection strategy for sour water stripping was single-point injection in the tower feed. This was more effective than single-point injection at the tower middle or bottom, and more effective than multiple point injection.

-- The optimum caustic injection strategy (in the tower feed) freed practically all of the fixed NH_3 and did not interfere with H_2S removal.

The API has also funded work by Dr. Grant Wilson at the Thermochemical Institute of Brigham Young University (BYU). The objectives of that program were:

- To obtain new and additional VLE data for the NH_3-H_2S-H_2O system. Since Van Krevelen's work was essentially at atmospheric pressure and 70-140 °F, BYU was to obtain data ranging from 150-250 psia and 175-250 °F. Whereas Van Krevelen's VLE data could only be extrapolated and used for NH_3/H_2S molar ratios above 1.5, the BYU results would provide VLE data applicable at any NH_3/H_2S molar ratio.
- To provide a correlation that would calculate system pH's as well as VLE data.
- To extend the VLE data base to include other species such as mercaptans, cyanides, phenols, CO_2 and others.

The BYU results have been published in a series of draft reports, the latest of which is dated May 1977(8). A final report is in preparation. The BYU results are summarized below:

-- New VLE data have been obtained as follows:

System	Data points
H_2S-H_2O	9
HCN-H_2O	8
C_2H_5SH-H_2O	6
NH_3-H_2S-HCN-H_2O	4
NH_3-H_2S-H_2O-Phenol	6
NH_3-H_2S-H_2O-Xylenol	6
NH_3-H_2S-H_2O	18*

(* 176-248 °F and 15-242 psia total pressure)

-- In general, when the BYU data points for the NH_3-H_2S-H_2O system are compared to temperature-extrapolated Van Krevelen data WHERE THE NH_3/H_2S MOLAR RATIO IS ABOVE 1.5 AND VAN KREVELEN IS THEREFORE APPLICABLE, the BYU and the Van Krevelen correlations agree within about 20 %. Any other comparisons at NH_3/H_2S molar ratios of less than 1.5 are meaningless(1).

-- The BYU data should yield a VLE correlation that would apply at any NH_3/H_2S molar ratio. Such a correlation should be very useful in designing sour water fractionators including both a rectifying and a stripping section. It would also be useful in designing high pressure (200 psia) sour water systems.

-- BYU has developed a VLE correlation based on their measured data as well as data from Van Krevelen and many other literature sources which is combined with a method of calculating system pH as well.

The BYU experimental data work has greatly extended our VLE data base, but it requires a complex computer program for application. In most cases, for typical refinery sour water strippers, the Van Krevelen VLE correlation as recently modified(3) still provides a simple and reliable design basis.

Having been associated on a consulting basis with almost all of the research programs discussed in this paper, it is my own opinion that the most useful aspect of all the work has been the determination of the optimum caustic injection strategy for freeing the fixed NH_3 in sour water strippers. It is also my opinion that the experimental VLE work at BYU will prove to be very useful.

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(3) Beychok, M. R., "Program Calculators For Design Study", Hydrocarbon Processing, Sept. 1976

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(6) Dobrzanski, L. T. and Thompson, W. J., "Performance Evaluation Of Sour Water Strippers", 76th Annual AIChE Meeting, Tulsa, March 1974

(7) Bomberger, D. C. and Smith, J. H., "An Experimental Study Of Ammonia Fixation In Sour Water Strippers", API Meeting, Chicago, May 1977

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DISCUSSION

N.F. Seppi: How much caustic is typically added to raw sour water stripper feed?

Milton Beychok: SRI tested caustic injection at the top, the middle and the bottom of their laboratory stripper, as well as combinations of those injection points. Their caustic injection rates ranged from 60% to 120% of the stoichiometric amount based on the fixed ammonia present. As I recall, 90% to 100% of the stoichiometric amount was enough to free and to remove essentially all of the fixed ammonia.

Ed Bienhoff: Are you indicating that there is a shift away from two-stage strippers where caustic is injected between stages?

Milton Beychok: I did not realize that I had even mentioned that aspect. As you know, some refiners have used two-stage strippers to remove the ammonia and the H_2S as separate streams and to dispose of them separately. Basically, those operations use two conventional strippers in series. Acid is injected into the first stripper to maximize the removal of H_2S and caustic is injected into the second stripper to maximize ammonia removal. Personally, I think that it is better to use one of the proprietary licensed processes for that purpose, such as Chevron's fractionating process of U.S. Steel's PHOSAM process. My reason for preferring those processes over the two-stage system with separate acid and caustic injection is that it must be quite difficult to achieve good pH control in the two-stage system without running into a lot of corrosion problems.

N.F. Seppi: I must have misunderstood you. Were you referring to caustic injection into a single tower or into the feed of the second tower of a two-stage system?

Milton Beychok: In terms of the SRI work, I was referring to a single conventional stripper with caustic injection into the feed entering that single stripper (i.e. the top of the column), or the middle of that stripper, or the bottom of that stripper as well as combinations of those injection points. Feed injection proved to be the best.

BIOGRAPHY Milton R. Beychok

Milton R. Beychok is a consulting Chemical Engineer in the field of environmental technology. He has a B.S. degree in Chemical Engineering from Texas A & M University, and he is a registered professional engineer in California and Texas. He is a Diplomate of the American Academy of Environmental Engineers and is a member of the AIChE, Air Pollution Control Association and the Water Pollution Control Federation. He has served on the California Water Quality Control Board ;and consulted from the EPA, the National Science Foundation and the National Commission on Water Quality. Prior, to entering private practice he was with Fluor Engineers & Constructors for 20 years.

TABLE 1

1972 SOUR WATER STRIPPER SURVEY*

PERFORMANCE

Average NH_3 removal = 78.1 % (50 towers reported)
Average H_2S removal = 95.8 % (51 towers reported)

TRAYED TOWERS

Average number of trays = 15 (44 towers reported)
Average number of trays, excluding three highest and three lowest values = 15

Average tray efficiency = 46 % (12 towers evaluated)
Average tray efficiency, excluding one highest and one lowest value = 45 %

PACKED TOWERS

Average packed height = 15 ft (14 towers reported)

STRIPPING STEAM

Average of all towers = 0.8 lbs/gal of raw feed
Average of all towers removing more than 90 % NH_3 = 1.2 lbs/gal of raw feed

TOTAL STEAM

Average of all towers = 1.1 lbs/gal of raw feed
Average of all towers removing more than 90 % NH_3 = 1.4 lbs/gal of raw feed

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API Publication No. 927, June 1973 (73 survey questionnaires)

TABLE 2

ALLOWABLE NH_3 CONTENT IN STRIPPED SOUR WATER TO MEET 1983 BATEA LIMITS

(Typical 125,000 BSD Refinery)

EPA category .... cracking
Process configuration 6.32
Process factor 1.09
Size factor 1.47

Stripped sour water = 300 gpm = 3,600,000 lbs/day

BATEA limits (30-day average):
BOD = 1.0 lbs/1000 bbls crude oil
NH_3-N = 1.2 lbs/1000 bbls crude oil

Variability factors:
BOD = 1.7
NH_3-N = 1.5

BATEA allowable discharges (equivalent annual averages):

BOD = (1.09)(1.47)(1.0)(125)/1.7 = 118 lbs/day
NH_3-N = (1.09)(1.47)(1.2)(125)/1.5 = 160 lbs/day

Assuming a biotreater removes 90 % of the BOD and consumes 4 lbs of Nitrogen/100 lbs of BOD removed*:

Nitrogen consumed = 118(0.9/0.1)(4/100) = 42 lbs/day
Nitrogen entering = 160 + 42 = 202 lbs/day

Assuming 70 % of Nitrogen entering the biotreater comes from the stripped sour water:

Allowable NH_3 in stripped water

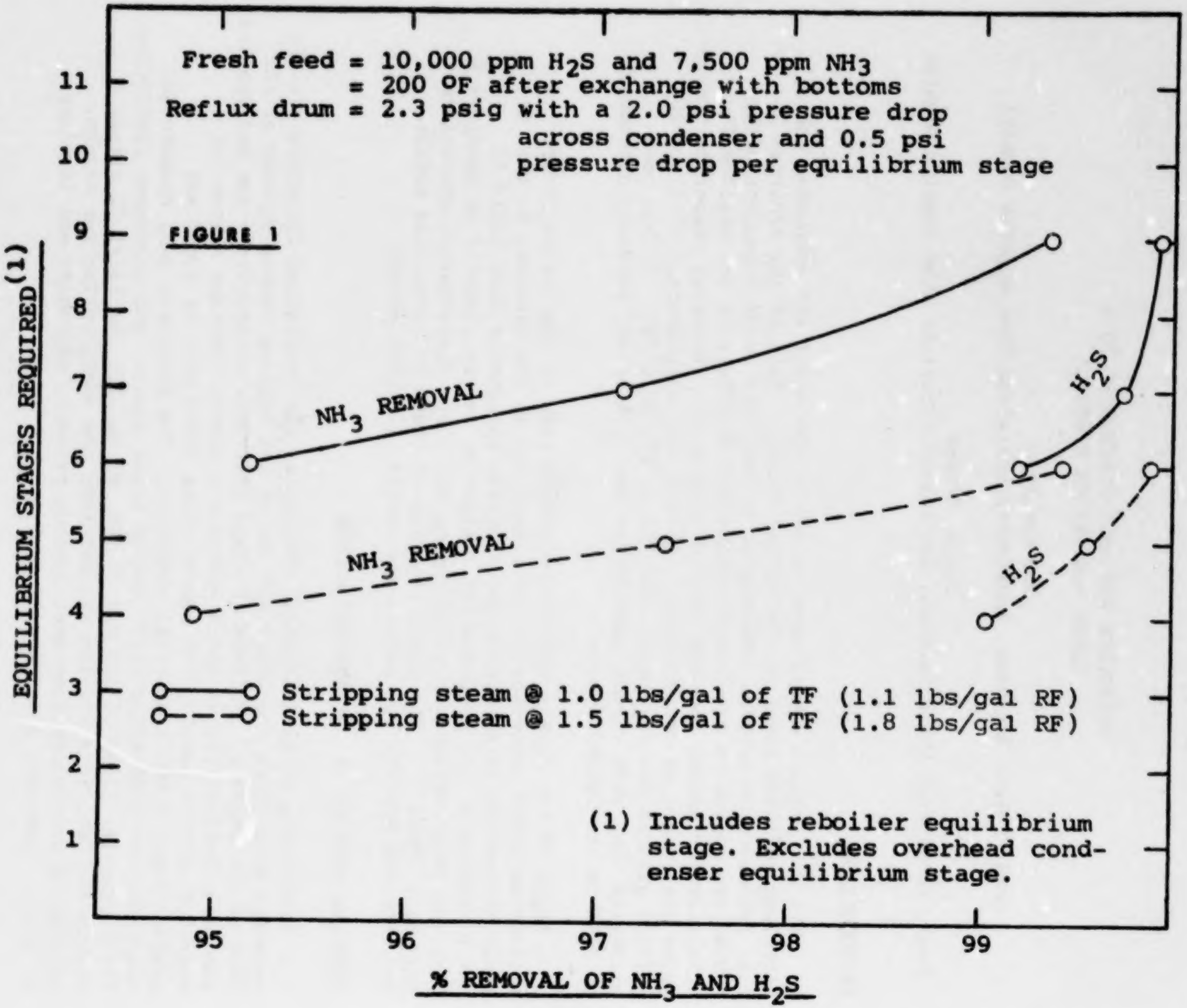
= 202(0.7/3.6)(17/14) = 48 ppm as NH_3

Repeating the above calculations for a range of values:

stripped sour water (gpm)	% of NH_3 entering biotreater coming from SWS	allowable ppm NH_3 in stripped water
300	90	61
300	70	48
300	50	34
350	90	53
350	70	41
350	50	29
		range: 30 to 60 ppm

* If only half of the BOD is removed in a biotreater, the range is 25 to 50 ppm

FIGURE 1



Fresh feed = 10,000 ppm H_2S and 7,500 ppm NH_3
= 200 °F after exchange with bottoms
Reflux drum = 2.3 psig with a 2.0 psi pressure drop across condenser and 0.5 psi pressure drop per equilibrium stage

(1) Includes reboiler equilibrium stage. Excludes overhead condenser equilibrium stage.

PETROLEUM REFINERY DISCHARGES TO A LARGE SANITATION DISTRICT

Irv Kornfeld
Lead Project Engineer, Sanitation Districts (Los Angeles County)

Jay G. Kremer
Head, Industrial Waste Section, Sanitation Districts (Los Angeles County)

INTRODUCTION

The Los Angeles County area is one of the major oil producing and petroleum refining areas in the United States. Half of the reported 26 U.S. petroleum refineries discharging to publicly owned treatment works (POTW) are served by the County Sanitation Districts of Los Angeles County (Districts or LACSD) sewerage system (Figure 1). Refinery industrial wastewater discharges to the Districts total in the neighborhood of 17 to 20 million gallons per day (mgd), (64,345 to 75,700 m^3/d). It has been estimated that this volume constitutes over 50% of all refinery discharges to POTW in the United States.

Eight of the larger refineries discharging to the Districts are refineries whose processes can be classified in EPA Category B; that is, those refineries with topping and cracking operations (see Table 1). The processes of the five smaller refineries can be classied in Category A; that is, those refineries with topping and crude distillation operations only (see Table 2). The crude capacity of these 13 refineries totals over 800,000 barrels per stream day (b/sd), (127,176 m^3/sd).

SEWERAGE SERVICE IN LOS ANGELES COUNTY

Consisting of 27 individual districts, the Sanitation Districts provide sewerage service to the major portion of Los Angeles County outside of the City of Los Angeles. Fifteen of these Districts collectively own and operate the Joint Outfall System which provides a common sewerage system for over 3.8 million people, 750 square miles (1943 km^2) of area, and approximately 8,000 industrial companies. The Districts own, operate and maintain over 1100 miles (1770 km) of trunk sewers, and treatment facilities for wastewater flows of 420 mgd (1,589,700 m^3/d). The local 72 cities within the Districts provide and maintain the small collection sewers. Methods of wastewater treatment include primary, secondary and tertiary at eleven treatment plant locations.

THE JOINT WATER POLLUTION CONTROL PLANT

All but one of the petroleum refineries discharge to the Districts' Joint Water Pollution Control Plant (JWPCP) located six miles inland from the Pacific Ocean, in the City of Carson. The tributary sewers to this plant accept primary and activated sludge from several upstream treatment plants, in addition to domestic and industrial wastewater. The JWPCP presently utilizes primary treatment with polymer addition and advanced solids recovery procedures to treat a daily average of 350 mgd (1,324,750 m^3/d) of wastewater, which includes approximately 70 mgd (264,950 m^3/d) of industrial flow. The petroleum refineries' wastewater discharge amounts to approximately 25% of this industrial flow and about 5% of the total JWPCP wastewater influent.

The JWPCP solid wastewater material, except for grit, is digested anaerobically. The digested material is processed by screening, centrifuging, and air drying for conversion to an innocuous end product suitable for use as fertilizer. The JWPCP wastewater effluent is discharged directly to the Pacific Ocean about two miles off-shore from the Palos Verdes Peninsula through a system of tunnels and submarine outfalls. A commitment has been made by the Districts and work is currently underway to convert the JWPCP to a full secondary biological treatment plant. Many components of refinery wastewater such as phenols, and oil and grease will be more adequately treated by such a plant.

THE DISTRICTS' INDUSTRIAL WASTE ORDINANCE

In 1972, requirements defined in the Federal Water Pollution Control Act Amendments (PL 92-500) and the State of California "Ocean Plan" mandated that the Districts establish a program which would control pollutant levels in treatment plant effluents. To meet the Districts' treated wastewater quality goals, control industrial pollutants, and to recover the true cost of wastewater treatment from industrial companies, the Districts adopted a Wastewater Ordinance on April 1, 1972.

This ordinance, which was amended on July 1, 1975, included a permit program for industrial dischargers to the sewerage system. Information required in the permits for major dischargers included:

1. Industrial process descriptions.
2. Industrial process equipment information and plans.
3. Description of wastewater pretreatment equipment.
4. Sewer plans of the industrial plant.
5. Pertinent wastewater constituent concentrations.
6. Wastewater flow volumes and methods of wastewater flow measurement.

7. Description of liquid waste materials disposed of other than to the sewerage system.

Wastewater characterization information required from the refineries includes the parameters listed in Table 3. The permit requirements for the petroleum refinery industry (SIC 2911) specify minimum wastewater pretreatment facilities of an oil-water separator and a sampling point.

THE INDUSTRIAL WASTE SECTION

The Districts' unit implementing the industrial waste regulatory program is the Industrial Waste Section. Permit processing, field inspection, and industrial waste engineering are the function designations of the three subsections of the Industrial Waste Section. Graduate civil, chemical or mechanical engineers fill over two-thirds of the 19 professional positions in this section. One function of the industrial waste engineering subsection is to provide technical support through a project engineer competent in a specific field of industrial wastewater engineering. One project engineer covers the oil producing and petroleum refining industries.

WASTE DISCHARGES PROHIBITED BY ORDINANCE

Listed in the Districts ordinance as prohibited discharges and applicable to wastewaters from petroleum refineries are the following:

1. Any gasoline, benzene, naptha, solvent, or fuel oil.
2. Any waste containing toxic or poisonous solids, liquids or gases.
3. Any waste having a pH lower than 6.0 or having any corrosive or detrimental characteristic that may cause injury to wastewater treatment or maintenance personnel.
4. Any solids or viscous substances of any size or in such quantity that they may cause obstruction to flow in the sewer or be detrimental to proper wastewater treatment plant operations.
5. Any rainwater, stormwater, groundwater, or street drainage.
6. Any water added for the purpose of diluting wastes which would otherwise exceed applicable maximum concentration limitations.
7. Any excessive amounts of petroleum or mineral based cutting oils (commonly called soluble oils) which form persistent water emulsions.
8. Any excessive concentration of non-biodegradable oil, petroleum oil or refined petroleum products.

9. Any waste with an excessively high concentration of cyanide.
10. Any unreasonably large amounts of undissolved or dissolved solids.
11. Any waste with excessively high BOD, COD or decomposable organic content.
12. Any strongly odorous waste or waste tending to create odors.
13. Any waste containing dissolved sulfides above a concentration of 0.1 milligram per liter.
14. Any waste with a pH high enough to cause alkaline encrustations on sewer walls or other adverse effects on the sewerage system.
15. Any waste having a temperature of 120°F or higher.
16. Any excessive amounts of deionized water, steam condensate, or distilled water.
17. Any waste containing substances which may precipitate, solidify or become viscous at temperatures between 50°F and 100°F.
18. Any blowdown or bleed water from cooling towers or other evaporative coolers exceeding 1/3 of the make-up water.
19. Any single-pass cooling water.

These regulations have had a major effect on the ability of Districts' treatment plants to handle refinery wastes and the type of pretreatment equipment required at each refinery.

INDUSTRIAL USER CHARGE

Prior to the advent of the Districts' industrial waste ordinance, the petroleum refineries and all other large industrial dischargers were charged only an ad valorem (property) tax for sewerage service. This tax, however, did not cover the true costs of industrial wastewater treatment. The Districts' ordinance established an industrial user charge or surcharge to obtain the revenue needed to meet federal law PL 92-500 requirements. Use was made of the charge parameters of total wastewater flow, chemical oxygen demand, suspended solids and peak flow in a Districts' surcharge formula (Table 4).

The surcharge rates for the last three fiscal years are given on Table 5. The flat rate charge of $230 to $250 per million gallons can be utilized by only industrial waste dischargers of less than 6 million gallons per year. However, this figure of $250 per million gallons is the approximate amount that a large refinery will pay the Districts for sewerage service.

The fiscal year 1975-76 ad valorem (property) taxes and surcharge from the refineries to the Districts totaled about $1,100,000 of which the surcharge portion amounted to about $715,000. The refineries' surcharges amounted to approximately 16% of all industrial waste surcharge payments received in fiscal year 1975-76.

SULFIDES AND THIOSULFATES

In the 10 years prior to promulgation of the Districts ordinance, a Districts' policy governing the use of trunk sewers provided that dissolved sulfides in wastewater discharged to the sewer must not exceed a concentration of 0.1 mg/l. The petroleum refineries, since the early 1960's, had treated wastewater containing high dissolved sulfides by oxidizing these sulfide compounds to thiosulfate.

In the early 1970's, new State of California discharge requirements for the Districts' JWPCP included more stringent bacterial standards. These standards required substantial chlorination of JWPCP effluent when large quantities of refinery thiosulfate was present. In order to maintain chlorination effectiveness, the Districts required that each refinery discharging to the Districts' system must reduce its thiosulfate level to not more than 50 mg/l as sulfur. The refineries were given a period of two years, until July 1, 1973, to complete the required construction for the reduction in thiosulfate concentration.

Only the refineries in the EPA Category B, which were high dischargers of thiosulfate, were affected. These refineries, totaling over 90% of all refinery discharges, accomplished the task of reducing thiosulfate by constructing sulfide strippers for refinery sour water streams. These sulfide strippers had a most significant effect in reducing overall pollutant concentrations discharged from the refineries.

OIL AND GREASE

Concentrations of mineral oil and grease greater than 75 mg/l are considered excesssive in industrial discharges to the Districts' system. Refinery wastewater dischargers are required, as a condition of permit approval, to pretreat so that the oil and grease content is below 75 mg/l. All major refineries have used a combination of "good housekeeping", improved oil water separators and dissolved air (or gas) flotation units to obtain adequate oil and grease removals.

RAINWATER

It is the policy of the Sanitation Districts that rainwater will not be permitted access to the Districts' sewerage system due to limited capacity, primarily designed for dry weather flows, (separate sanitary sewerage system). In certain situations, where discharge to the storm sewer is not feasible, refineries are permitted to discharge rainwater to the sewer. Rainwater permitted to be discharged with industrial wastewater during a rain storm is limited to the first 0.1 inch (2.54 cm) of rainwater over the relevant surface area. Normally, rainwater diversion devices discharge storm flow to surface drains after 0.1 inch (2.54 cm) of rain has fallen. If greater than this amount of rainwater is too polluted for discharge to a storm drain, it may be stored on the refinery property during the rain storm for later discharge to the sewer. Discharge to the Districts sewerage system can only be made 24-hours after the cessation of rainfall and then only during the off-peak hours of sewer flow, (10:00 p.m. to 8:00 a.m.).

TOXIC WASTEWATER CONSTITUENTS

Limits for the discharge of toxic pollutants, mainly heavy metals, were presented to industry on July 1, 1975, with an enforcement date, after an eighteen-month implementation period, of January 1, 1977 (see Table 6). The Districts believe that these limits with some minor modifications will allow the Districts to comply with it's NPDES permit requirements for toxic pollutants discharged from its treatment plants. The refineries' existing wastewater discharges are generally in compliance with these toxic wastewater constituent limits. Typical concentrations of these materials in refinery effluent are shown in Table 7.

REFINERY DISCHARGE IMPROVEMENTS

A significant reduction was noted in refinery wastewater pollutants in 1974 following the start up of refinery sour water strippers and the resultant reduction in wastewater thiosulfate to levels of less than 50 milligrams per liter. Tables 8 and 9 indicate typical wastewater quality at the same category refineries during 1972-73. Table 10 and 11 indicate typical wastewater quality at the same category refineries during 1975-76. The mass emission totals and percentage reductions for refinery wastewater pollutants between the years 1972-73 and 1975-76 are listed in Table 12.

In addition to thiosulfate, significant reductions were obtained in other refinery constituent levels, including COD, ammonia, phenols, and oil and grease. During the three year period, the refineries improved their primary treatment facilities and upgraded their environmental wastewater management efforts. These activities served to significantly reduce refinery wastewater pollutant levels.

Reduction in refinery pollutant levels coincided with significant reductions in BOD levels, about 70 mg/l, in the influent to the JWPCP. An investigation determined that these reduced BOD levels were mainly attributable to the decrease in refinery thiosulfate discharges.

It has been estimated that, since 1972, the cost to the LACSD refineries for capital wastewater pretreatment improvements has amounted to over 20 million dollars. Thiosulfate reduction, which mainly included new sour water sulfur stripping facilities, accounted for approximately

80 percent of these costs.

REFINERY WASTEWATER PRETREATMENT SYSTEMS

Pretreatment of wastewater at the refineries discharging to the Districts sewerage system involves mainly advanced primary treatment. A primary treatment system for a Category B refinery includes a sour water stripper, a sour water oxidizer, an oil water separator, and a dissolved gas or air flotation unit. A typical pretreatment system for a large refinery is shown on Figure 3. Small Category A refineries have nearly the same pretreatment systems except the sour water stripping capability is usually not included. The small refineries, for the most part, refine low-sulfur crude which does not generate a high-sulfide wastewater.

Three of the large refineries discharging to the Districts' system are able to discharge a portion of their low pollutant wastewater streams to a storm water channel which flows to the Los Angeles Harbor area. These channel discharges are under the jurisdiction of the local California State Water Quality Control Board. The Board limits the mass emission of pollutants, including BOD and oil and grease, which can be discharged into a storm water channel.

REFINERY ODORS

The improvements in refinery pretreatment systems helped reduce odor problems in the Districts' trunk sewers and in treatment plants receiving refinery wastewater. One problem prevalent in the past was refinery odors being released in a Districts' treatment plant.

With one company's cooperation, an in-plant refinery wastewater survey was initiated in order to determine if an odorous refinery wastewater stream could be selectively separated and treated for odor removal prior to sewer disposal. The refinery, at the time of investigation, discharged approximately 5 percent of the influent received at the Districts' Los Coyotes Water Reclamation Plant (LCWRP), a secondary treatment plant. At the time of the survey, the refinery did not have a sour water stripper and all sulfides were oxidized to thiosulfate.

It was found that the sour water oxidizer, operated for wastewater sulfide removal, was the refinery's major existing odor removal facility. Also, selectively removing particularly odorous sour water streams from the total refinery wastewater was not practical as over 60 percent of the refinery sour water streams included highly odorous sulfide concentrations. The installation of a sour water stripper facility, which could reduce ammonia, sulfide, and thiosulfate discharges, was found to result in substantial wastewater odor reductions. After the refinery's sour water stripper began operation, wastewater odors at the LCWRP were significantly reduced. Optimum stripper operation required removing a particularly odorous refinery spent caustic stream from sewer discharge and truck transportation of it to a landfill for disposal.

PETROLEUM REFINING PRETREATMENT STANDARDS

The Environmental Protection Agency (EPA) established petroleum refinery pretreatment standards (Part 419, Federal Register, March 23, 1977) in an interim final form for pollutants discharged to POTW from existing sources. Established were two sets of pretreatment standards. The first set, known as the prohibited discharge standards, is for control of gross problems such as the discharge of flammable materials or wastes that could plug sewers. The Districts' Wastewater Ordinance also prohibits the discharge of such materials to the sewer system. The second set of pretreatment standards establishes numerical limits on ammonia and oil and grease and suggests local restrictions on chromium sulfide and phenol.

The regulations established a maximum one-day concentration of 100 milligrams per liter (mg/l) for ammonia and 100 milligrams per liter for oil and grease allowed to be discharged by petroleum refineries to POTW. In addition, guidance was provided to the operators of POTW for control of chromium, sulfide, and phenolic compounds,which may prove harmful to or not be adequately treated by the POTW. The EPA recommended, however, that sulfides, phenols, and chromium be controlled only as needed by the local agency.

The Districts commented on the development document which established these regulations. It was recommended that the EPA either propose that sewerage agencies receiving refinery waste establish suitable local source control programs, or that any EPA limits be established uniquely for each of the 13 sewerage systems receiving such wastes. It is believed that sewerage agencies such as the Sanitation Districts have the staff and technical competence to operate a cost effective industrial source control program and should be given the total responsibility for such a program.

Impact on the Districts and the local petroleum industry for the items prohibited is minimal as the Districts' ordinance has already established most of the standards. The mean concentrations of oil and grease, and ammonia in the refinery studies made by EPA were stated to be well below the maximum pretreatment standard of 100 mg/l. This is not true for all refineries discharging to the Districts' sewerage system as two or three may discharge daily ammonia levels in excess of 100 milligrams per liter. If the Districts' treatment plants can meet the required NPDES permit conditions for ammonia discharge, it is not cost effective to require more severe refinery ammonia restrictions than needed for environmental protection. All of the Districts' refineries are required to discharge oil and grease below a daily level of 75 (<100) milligrams per liter.

SUMMARY

The Sanitation Districts of Los Angeles County provide sewerage service for 13 (50%) of the 26 U.S. refineries reported to be discharging to publically owned treatment works (POTW). Eight refineries are classified in EPA Category B and five in Category A. Total refinery capacity is 800,000 barrels per stream day (127,176 m^3/sd) with a wastewater discharge of about 17 to 20 million gallons per day (64,345 to 75,700 m^3/d).

The Sanitation Districts have been able to satisfactorily treat municipal wastewaters containing significant quantities of refinery wastes. Wastewater discharge requirements for refineries have been established by a Districts ordinance. This has resulted in wastewater pretreatment installations at local refineries costing over 20 million dollars. Most major refineries have pretreatment equipment which includes a sour water stripper, a sour water oxidizer, an oil-water separator, and a dissolved air (or gas) flotation unit.

A significant improvement in the quality of wastewater discharged by refineries has occurred in the last few years. Installation of improved pretreatment equipment by the refineries has significantly reduced some problems at Districts' treatment plants such as high odor levels and high wastewater organic content.

In the Sanitation Districts area, some pretreatment regulations for refineries are quite stringent, such as 0.1 mg/l of dissolved sulfide and 75 mg/l of oil and grease. Local conditions require that these limits be more severe than proposed by EPA in the recently published pretreatment regulations. Conversely, it appears that the EPA pretreatment limit of a one-day maximum concentration of 100 mg/l of ammonia from refineries may not be required for meeting pollution control goals.

The Sanitation Districts have requested that EPA permit responsible local sewering agencies such as the Districts to establish and enforce its own industrial pretreatment regulatory program. Such a program, aimed at meeting required receiving water quality, would comply with pollution control goals without placing an excessive cost burden on industry.

DISCUSSION

Randy Buttram: Can a limited amount of storm water be discharged along with normal process effluent during a storm?

Irv Kornfeld: Rainwater permitted to be discharged with industrial wastewater is limited to the first 0.1 inch (0.254 cm) of rainwater over the relevant surface area. It is the policy of the Districts that rainwater will not be permitted access to the Districts' sewerage system. This is because the system has limited capacity as it is primarily designed for dry weather flows. However, in certain situations where discharge to a storm sewer is not feasible, refineries are permitted to discharge rainwater to the sewer 24-hours after cessation of rainfall during the off-peak hours of sewer flow; that is, between 10:00 p.m. and 8:00 a.m.

BIOGRAPHIES

Irv Kornfeld is a Lead Project Engineer in the Industrial Waste Section of the Sanitation Districts of Los Angeles County. He holds a B.S. degree in Mechanical Engineering from the Illinois Institute of Technology and a M.S. degree in Civil Engineering from the California State University at Long Beach. He is a Registered Mechanical and Civil Engineer in the State of California and a member of ASCE and WPCF. Mr. Kornfeld has been with the Sanitation Districts since 1972 and has prior employment with engineering consultants and contractors to the petroleum refining industry.

Jay G. Kremer is Head of the Industrial Waste Section of the Sanitation Districts of Los Angeles County. He has a B.S. degree in Civil Engineering from Northwestern University, a M.S. degree in Sanitary Engineering from the Illinois Institute of Technology and a Masters of Public Administration degree from the University of Southern California. He is a registered Civil Engineer in California and a member of ASCE, WPCF and AAEE. He has been with the Sanitation Districts since 1963 and previously worked for various consulting engineer and governmental agencies.

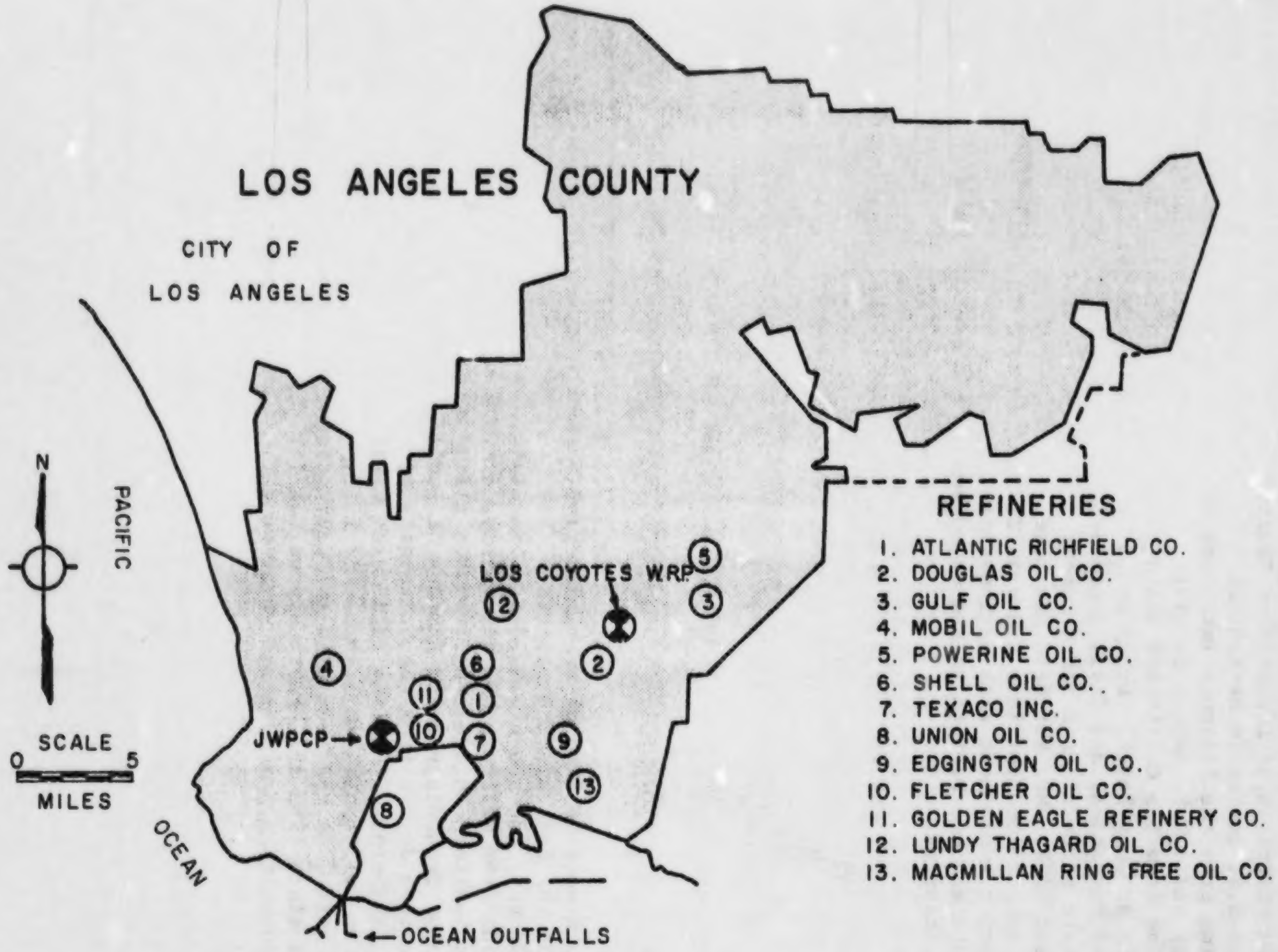
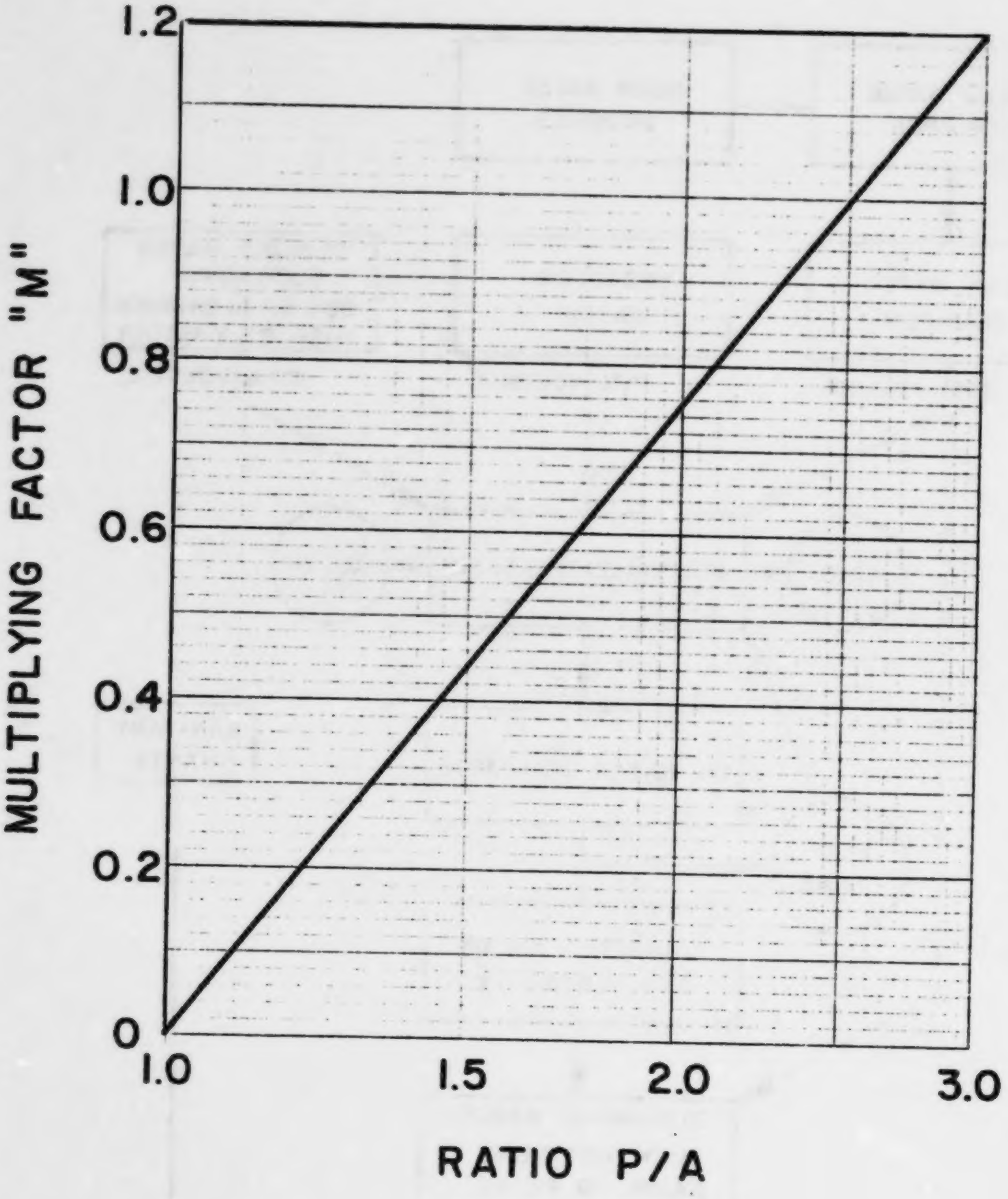


FIG. I. SANITATION DISTRICTS OF LOS ANGELES COUNTY PETROLEUM REFINERY LOCATIONS



NOTE: Mathematical formula for "M" is: $M = 2.5 \log(P/A)$

FIG. 2. VALUES OF MULTIPLYING FACTOR "M"

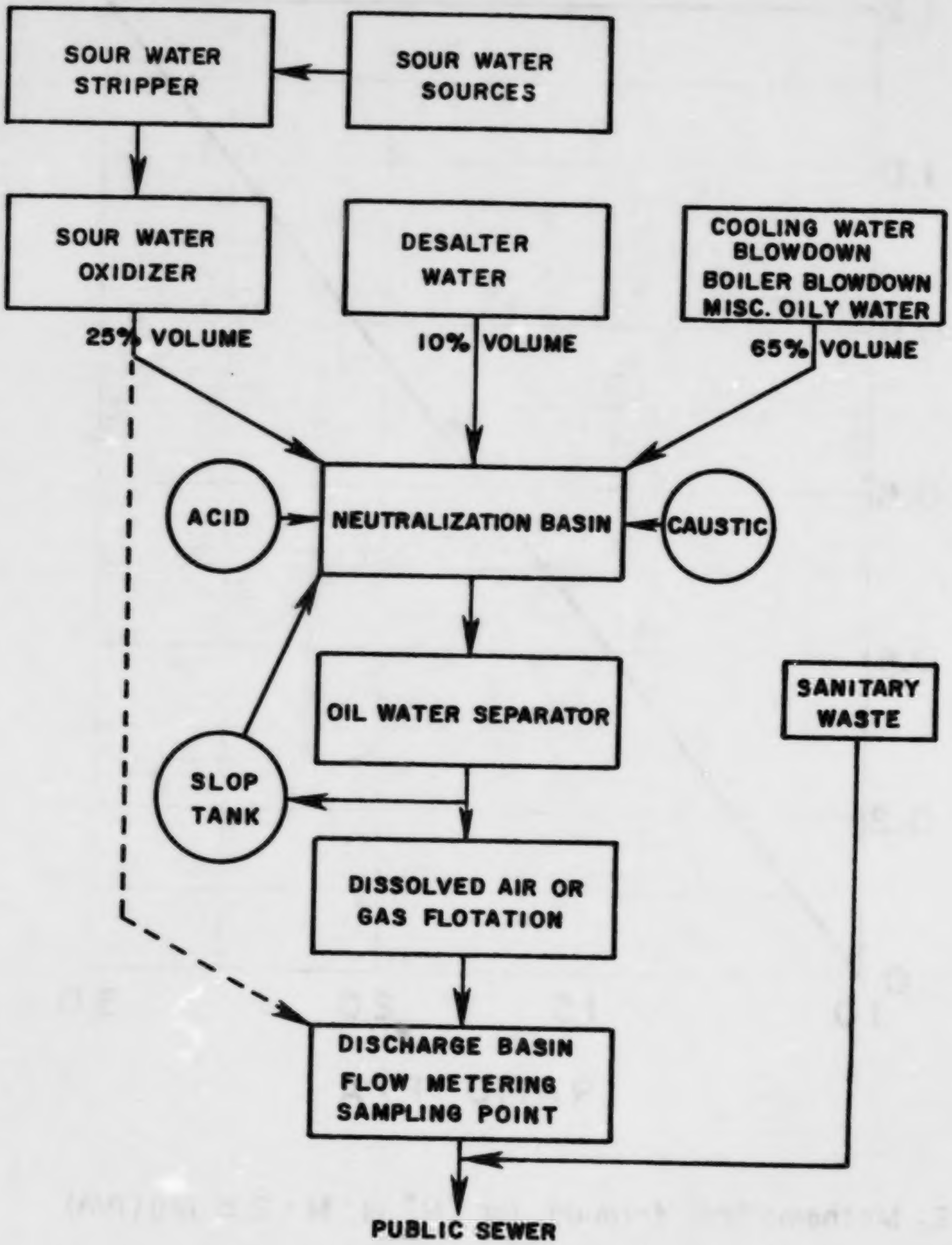


FIG. 3. TYPICAL LARGE REFINERY WASTEWATER PRETREATMENT SYSTEM

TABLE 1 REFINERIES DISCHARGING TO THE LACSD, CATEGORY B (TOPPING AND CRACKING PLANTS)

Refinery	Location	Crude Capacity b/sd	Wastewater Discharge mgd	
Atlantic Richfield Co.	Carson	186,000	> 4.0	< 6.0
Douglas Oil Co.	Paramount	48,000	> 0.2	< 0.5
Gulf Oil Co.	Santa Fe Springs	53,800	> 0.4	< 0.7
Mobil Oil Co.	Torrance	131,000	> 3.0	< 5.0
Powerine Oil Co.	Santa Fe Springs	46,000	> 0.2	< 0.3
Shell Oil Co.	Carson	93,000	> 2.0	< 4.0
Texaco, Inc.	Wilmington	79,000	> 0.6	< 0.8
Union Oil Co.	Wilmington	111,000	> 3.0	< 5.0
	Total	747,800	>13.4	<22.3

Metric Conversion

m^3/d = (mgd)(3,785)

TABLE 2 REFINERIES DISCHARGING TO THE LACSD, CATEGORY A (TOPPING PLANTS)

Refinery	Location	Crude Capacity b/sd	Wastewater Discharge mgd	
Edgington Oil Co.	Long Beach	31,000	>0.10	<0.30
Fletcher Oil & Refinery Co.	Carson	20,000	>0.05	<0.10
Golden Eagle Refinery Co.	Carson	13,000	>0.04	<0.07
Lunday-Thagard Oil Co.	South Gate	8,100	>0.02	<0.06
Macmillan Ring Free Oil Co.	Signal Hill	12,200	>0.05	<0.08
	Total	84,300	>0.26	<0.61

Metric Conversion

m^3/d = (mgd)(3,785)

TABLE 3 PETROLEUM REFINERIES WASTE CHARACTERIZATION

Parameter	Quantity Values
Flow (Total)	gals/day
Flow (Peak)	gals/day
COD	mg/l
Suspended Solids	mg/l
pH	units
Ammonia (N)	mg/l
Oil and Grease	mg/l
Phenols	mg/l
Thiosulfate (S)	mg/l
Arsenic	mg/l
Cadmium	mg/l
Chromium	mg/l
Copper	mg/l
Lead	mg/l
Nickel	mg/l
Zinc	mg/l
Cyanide	mg/l

TABLE 4 LACSD SURCHARGE

$$\text{Surcharge} = a(V) + b(COD) + c(SS) + dM(P) - TAX$$

and where surcharge equals net annual industrial wastewater treatment surcharge, in dollars. No refund is made if a negative number results.

V = Total annual volume of flow, in millions of gallons.
COD = Total annual discharge of chemical oxygen demand in thousands of pounds.
SS = Total annual discharge of suspended solids in thousands of pounds.
P = Peak discharge rate over a 30 minute period, occurring between the hours of 8:00 a.m. and 10:00 p.m.
A = Average discharge rate, determined by dividing (V) by the total annual hours of operation and working time for the industrial discharger converted to gallons per minute.
a, b, c & d = Unit charge rates adopted annually by the individual District based upon the projected annual total cost of wastewater collection, treatment and disposal, in dollars per unit.
M = A multiplying factor accoumting for increased Districts cost to high ratios of industrial discharge to obtain flow rates (P/A). Factor M is obtained from Figure 2.
TAX = The annual ad valorem taxes paid to the Districts during the accrual years on land or property utilized for the generation of industrial wastewater, in dollars.

TABLE 5 INDUSTRIAL WASTEWATER TREATMENT SURCHARGE RATES

Unit Rate	Parameter	Surcharge Rates		
		1974-75	1975-76	1976-77
a	Volume Millions of gallons per year	$104.00	$104.00	$127.00
b	COD Thousands of pounds per year	$ 6.25	$ 6.25	$ 6.60
c	Suspended Solids Thousands of pounds per year	$ 14.25	$ 14.25	$ 16.10
d	Peak Flow Gallons per minute	$ 18.75	$ 12.00	$ 14.60
Flat Rate Charge	Volume Millions of gallons per year	$230.00	$230.00	$250.00

TABLE 6 LACSD INDUSTRIAL WASTEWATER EFFLUENT LIMITATIONS FOR JOINT OUTFALL DISTRICTS

Constituent	Phase I Control Period (mg/1)
Arsenic	3
Cadmium	15
Chromium (Total)	10
Copper	15
Lead	40
Mercury	2
Nickel	12
Silver	5
Zinc	25
Cyanide (Total)	10
Total Identifiable Chlorinated Hydrocarbons	Essentially None

TABLE 7 TYPICAL REFINERY HEAVY METALS DISCHARGE LEVELS 1975-76 (typical day)

Constituents	Concentrations in mg/l
Arsenic	0.01
Cadmium	0.01
Chromium	1.1
Copper	0.06
Lead	0.11
Nickel	0.08
Zinc	0.41
Cyanide	0.85

TABLE 8 LACSD REFINERY DISCHARGE LEVELS
1972-73 (Typical Day)
Category B Refineries

Refinery	A		B		C	
Flow mgd	4.968		0.479		3.297	
	mg/l	lb/day	mg/l	lb/day	mg/l	lb/day
COD	1,426	59,083	2,640	10,546	3,205	88,128
Suspended Solids (SS)	27.5	1,139	97	388	108	2,970
pH	7.4	---	8.9	---	11.5	---
Ammonia (N)	895	37,082	1,075	4,294	1,162	31,951
Oil & Grease	25	1,036	165	659	122	3,355
Phenols	460	19,059	80	320	3.93	108
Thiosulfate (S)	783	32,442	865	3,455	2,113	58,101
Chromium (Cr)	0.445	18.45	1.10	4.39	1.22	33.54

Metric Conversion

kg = (lb)(0.454)

TABLE 9 LACSD REFINERY DISCHARGE LEVELS
1972-73 (Typical Day)
Category B Refineries

Refinery	D		E		F	
Flow mgd	4.034		0.739		3.958	
	mg/l	lb/day	mg/l	lb/day	mg/l	lb/day
COD	2,956	99,450	12,702	78,285	1,795	59,252
Suspended Solids (SS)	595	20,117	30	185	8	264
pH	8.7	---	8.3	---	6.9	---
Ammonia (N)	181	6,089	3,280	20,215	776	25,615
Oil and Grease	460	15,476	50	308	9	297
Phenols	1,617	54,401	155	955	30	990
Thiosulfate (S)	688	23,148	2,380	14,669	1,427	47,105
Chromium (Cr)	1.06	35.66	0.258	1.59	1.34	44.23

Metric Conversion

kg = (lb)(0.454)

TABLE 10 LACSD REFINERY DISCHARGE LEVELS
1975-76 (Typical Day)
Category B Refineries

Refinery	A		B		C	
Flow, mgd	5.513		0.530		4.028	
	mg/l	lb/day	mg/l	lb/day	mg/l	lb/day
COD	774	35,587	746	3,297	1,093	36,717
Suspended Solids (SS)	11	506	49	217	48	1,612
pH	10.6	---	---	---	9.8	---
Ammonia (N)	35	1,609	51	225	39	1,310
Oil and Grease	31	1,425	47	208	54	1,814
Phenols	32	1,471	14	62	76	2,553
Thiosulfate (S)	11	506	29	128	28	941
Chromium (Cr)	0.78	36	0.9	4	1.05	35

Metric Conversion

kg = (lb)(0.454)

TABLE 11 LACSD REFINERY DISCHARGE LEVELS
1975-76 (Typical Day)
Category B Refineries

Refinery	D		E		F	
Flow, mgd	2.918		0.703		3.299	
	mg/l	lb/day	mg/l	lb/day	mg/l	lb/day
COD	1,223	29,763	4,150	24,332	282	7,759
Suspended Solids (SS)	53	1,290	47	275	32	880
pH	8.5	---	6.8	---	7.1	---
Ammonia (N)	547	13,312	162	950	92	2,531
Oil and Grease	96	2,336	120	704	5	138
Phenols	78	1,898	178	1,044	18	495
Thiosulfate (S)	18	438	31	182	30	825
Chromium (Cr)	1.1	27	0.09	0.5	0.69	19

Metric Conversion

kg = (lb)(0.454)

TABLE 12 LACSD REFINERY DISCHARGE LEVELS (TYPICAL DAY), Totals of Refineries A, B, C, D, E, F (Over 90% of LACSD Refinery Flow)

		1972-73	1975-76	% Reduction
Flow	mgd	17.48	17.00	
COD	lb/day	394,744	137,445	65
Suspended Solids (SS)	lb/day	25,063	4,780	81
Ammonia (N)	lb/day	125,246	19,937	84
Oil and Grease	lb/day	21,131	6,625	69
Phenols	lb/day	75,833	7,523	90
Thiosulfate (S)	lb/day	178,920	3,020	98
Chromium (Cr)	lb/day	137.86	121.50	12

Metric Conversion

kg = (lb)(0.454)

SESSION VII

POWDERED ACTIVATED CARBON

Chairman

Thomas P. Meloy

Director, Industrial and Extractive Processes
Division, U.S. E.P.A., Washington, D.C.

Speakers

Francis L. Robertaccio
"Combined Powdered Activated Carbon Treatment-Biological Treatment: Theory and Results"

Colin G. Grieves and Michael K. Strenstrom

Joe D. Walk and James F. Grutsch

"Powdered Activated Carbon Enhancement of Activated Sludge for BAT Refinery Wastewater Treatment"

Paschal B. DeJohn and James P. Black
"Case Histories: Application of PAC in Treating Petroleum Refinery Wastes"

James F. Dehnert
"Case History: Use of PAC With a Biodisc-Filtration Process"

BIOGRAPHY Thomas P. Meloy

Dr. Thomas P. Meloy is Director of the Industrial and Extractive Processes Division, Office of Research and Development, U.S. Environmental Protection Agency. He holds an A.B. and B.S. respectively from Harvard and MIT as well as a Ph.D. from MIT. Formerly, he was Director of Engineering Division at the National Science Foundation and Vice-President for Research and Development at Meloy Laboratories. His specialized field is particulate systems. This fall he will become the Benedum Professor at West Virginia University.

"COMBINED POWDERED ACTIVATED CARBON - BIOLOGICAL TREATMENT: THEORY AND RESULTS"

Francis L. Robertaccio
Senior Engineer
E. I. du Pont de Nemours & Co., Inc.
Central Research and Development Department
Wilmington, Delaware

The purposes of this paper are: to acquaint you with an overview of some of the theoretical aspects of the combined powdered activated carbon-biological treatment process, and to present recent start-up experiences and results from the 1.5 x 10^5 M^3/day installation based on the process at the Du Pont Chambers Works Plant in Deepwater, New Jersey.

PACT is Du Pont's name for a patented process for purification of sewage and/or industrial wastewater which comprises subjecting the wastewater to an aerobic biological treatment process in the presence of powdered activated carbon(1) (Figure 1). The aerobic biological treatment vessel(s) can have many geometric configurations. Single or multiple reactors can be used. The reactors can be plug flow, completely mixed, or somewhere in between. Powdered activated carbon addition is compatible with activated sludge, contact stabilization, or aerated lagoon systems; that is, any process in which the carbon can be suspended. The rate of powdered activated carbon addition for a given wastewater is a function of the effluent quality desired. When the rate of addition is expressed in terms of weight of carbon added per unit volume of incoming wastewater, the rate becomes a function of the type of carbon used.

In addition, certain internal process controls such as the solids retention time, or sludge age, can be changed to influence the rate of application of a given type of carbon to produce a desired result.(2) Some of these relationships are illustrated in Figure 2. Here sludge age and carbon dose are shown as variables affecting effluent quality as measured by the total organic carbon (TOC) test. All data points represent treatment conditions by which the effluent BOD of the industrial wastewater tested was reduced to negligible concentration. The effluent TOC is shown to be reduced by an independent increase in either the sludge age or the carbon dose. Note that the improvement in effluent quality, by increasing sludge age, is less apparent when carbon is absent. We have long postulated this phenomena results because the adsorbed microorganisms have the sludge age rather than the relatively shorter hydraulic detention time to biodegrade adsorbed and difficult-to-degrade molecules. It is important to recognize the economic advantage associated with the ability to biodegrade these materials in the biological reactor as an inherent advantage of the process.

The alternative for this type of effluent quality improvement is a more expensive add-on granular carbon adsorption step.

Table 1 illustrates the effectiveness of using carbon as an adsorbent in a biological reactor.(3) The table shows the dissolved organic carbon (DOC) removal from a PACT unit and comparable data from a biological unit. Also shown is the combined removal obtained from a separate adsorption of the biological unit effluent using the same type and quantity of carbon used in the PACT unit. The same carbon combined with bacteria in the PACT unit removed more DOC and exceeded the quantity expected from separate isotherm determinations.

Of course, as more molecules are biodegraded, adsorption sites are filled with molecules that are more biorefractory and a more rigorous form of regeneration is needed if the spent carbon is to be reused. Alternatively, more active carbons (i. e., higher surface area) can be used in throw away doses. Economic considerations grouped as various capital and operating expenses dictate the choice. To some extent the economics are strongly influenced by the carbon usage rate, however, site specific factors such as the local costs of alternative sludge disposal methods must be considered. At the PACT treatment facility for Chambers Works we will thermally regenerate carbon from PACT sludge but wet oxidation can also be used.

The heart of the PACT system is a matrix of microorganisms and powdered activated carbon. Figure 3 shows the matrix.(2) The photo on the left is powdered activated carbon in the water; the photo on the right the PACT matrix. The PACT matrix has some interesting properties.

First, the carbon acts as a weighting agent. Sludge settling rates are vastly improved as illustrated in the series of pictures in Figure 4. Activated sludge and PACT mixed liquor were taken from treatability units operating on the same wastewater at the same sludge age. The series of photographs are taken at different elapsed settling times shown on the timer in the background. Note that the PACT sludge settles better and has a clearer supernatant. The PACT sludge also compacts very well. The PACT sludge had a mixed liquor suspended solids concentration of 7700 mg/l (about 65% carbon) and a sludge volume index of 20 cc/g. The activated sludge had a mixed liquor concentration of 2400 mg/l and a sludge volume index of 46. We feel that the improved sludge settling, achieved by simple carbon addition can result in the processing of more wastewater through existing hydraulically overloaded treatment plants. This is often a viable alternative to rather expensive capital equipment expansion programs to accomplish similar results. Of course, carbon addition will improve effluent quality at the same time. A new treatment plant can incorporate this advantage in its design by substantially reducing the size of secondary clarification. Another illustration of the improved settling of PACT sludge is shown in Figure 5. Here the initial settling velocity of activated sludge is compared at various concentrations to a family of PACT sludge curves at two carbon levels and two temperatures. The numbers on the PACT labeled curves are the application rates for carbon in mg/l.

While on the topic of sludge handling, it should be mentioned that PACT sludge dewaters much more readily than conventional activated sludge. The manifestation of this property is reduced size of sludge dewatering equipment. The need to dewater more sludge as a result of the presence of carbon is offset by reduced cycle times. Figure 6 compares the specific resistance of activated sludge to two PACT sludges at different carbon feed doses.(3)

A second property of the PACT sludge matrix is that it contains an effective adsorbent. We have already explored one aspect of the role of the adsorbent - removal of biorefractory organic compounds - in the discussion of carbon dose and its relationship to sludge age. In that discussion the effluent total organic carbon content was a gross measure of biorefractory material. More specific measures of biorefractory materials which might require control in specific instances include materials contributing to final effluent color, oil and grease, surfactants, chlorinated hydrocarbons, phenols and toxicity to fish or other trophic level measures of toxicity in receiving waters. No matter how you care to measure, or are told to measure these biorefractory materials,it is apparent PACT can control these substances to levels beyond the capability of conventional biological systems. In complex waste situations control of these substances at the PACT treatment plant is often a more viable alternative than biological systems followed by granular activated carbon columns or source treatment.

Sometimes biorefractory materials are as much, or more of a problem within a biological system as they are in its final effluent. Examples include materials toxic or inhibitory to biological reactor microorganisms, materials that are periodically present in high concentrations (shock loads), or materials that cause severe foam, odor, or bulking sludge. Unlike post-biological separate granular activated carbon treatment, the presence of carbon in the aerator often controls these in-process problems as well as those normally associated with the biologically treated effluent. Over the years, we have had a difficult time sustaining bench scale biological treatability units on Chambers Works wastewaters due to the periodic presence of toxic or inhibitory materials.(4) However, PACT treatability units operated in parallel did not experience similar upsets. As a result of this property of the PACT process the full scale PACT facility at Chambers Works has no upstream equalization. We have even spiked Chambers Works wastewater with various toxic substances including pentachlorophenol (190 l/min. pilot plant test) and found the PACT system can sustain efficient operation when the conventional biological system completely fails. Ferguson, et al , reported similar findings in shock loading tests involving trichlorophenol.(5)

There are two intertwining reasons to consider any waste treatment process: technical merits and economics. We have touched upon the technical merits of the PACT process and summarized them in Table II. In most instances any one of the technical merits may be sufficient reason to consider PACT. In most instances a number of technical merits must be simultaneously applied to the consideration of the process at a specific site. The resulting matrix of reasons results in a difficult appraisal of the full value of the use of the PACT process versus alternative processes. Some of the economic considerations are shown in Table III. At Du Pont we are convinced PACT is a versatile, economic and technically viable process. We have about 100 man years experience in PACT process research and development. At the Chambers Works facility which will be described next, we feel PACT represents a $7 million capital savings and a $5 million/year operating cost savings (1972 dollars) over the next best alternative which was granular carbon treatment followed by activated sludge.(6)

The full scale PACT facility at Chambers Works has been in a start-up phase since mid-November 1976, and it proceeded smoothly through the coldest winter in decades. The liquid train is on line and the solids handling train is expected to be fully operational fairly soon. During March 1977 a half full flowrate test, and during early May a full flowrate test were conducted. This portion of this paper will highlight the start-up operation and describe results of the tests.

Figure 7 shows the major components of the PACT portion of the Chambers Works treatment plant. Construction of the PACT facility started in February 1974 and was completed in December 1976 at an estimated capital cost of $22.5MM. Primary effluent is split equally to each of three 15MM liter aeration tanks as is the recycled PACT sludge. Five 1,000 hp blowers supply air to static mixers in the aerators. Effluent from the aerators is conveyed to the clarifier flowsplitter and then to two secondary clarifiers. Treated effluent (overflow) is discharged to a basin and then to the Delaware River. Secondary clarifier underflow is returned to the aeration tanks via two 2 meter screw pumps. This part of the system constitutes the "liquid train" and includes feed and unloading facilities for carbon, phosphoric acid and polymer.

Waste sludge can be removed from either the mixed liquor or recycle lines and is pumped to a sludge thickener where it is settled to 7 ± 2 weight percent solids. The thickener underflow serves as a feed stream for the filter press which is designed to produce a 35 weight percent dry solids PACT cake. The cake is mechanically conveyed to a five hearth furnace where it is dryed, the biomass incinerated, adsorbed organics pyrolyzed and the powdered carbon in the sludge regenerated for reuse. The furnace off-gases pass through two scrubbers and an afterburner before being discharged to atmosphere. The dry, regenerated carbon recovered off the bottom hearth is slurried, acid washed, and returned to the carbon feed tanks for recycle to the process. No waste sludge is produced. This part of the system is called the "solid train".

The liquid train startup became evident in November 1976 when 2.7×10^5 kg of powdered carbon and 2.0×10^5 kg of bacterial solids were added to one aerator. Water temperature at the time was 11-15°C. During January a second aerator and clarifier were brought on line. During February the carbon regeneration startup began and during March the sludge press was brought on line. The more important operating problems encountered and solved during startup have been presented in a recent paper by Flynn.(7) The problems were of the type found with the startup of a conventional activated sludge process, that is, they were not at all related to the uniqueness of the PACT process. These problems went through the classic problem solving stages - initial definition, questioning of assumptions, hypothesis forming, reobservation of the problem in some cases, implementation of a solution and feedback on the success of the solution.

In March a half-full flowrate test was conducted. Table IV compares operating conditions, feed and effluent quality for the full scale PACT facility and various bench scale controls. The effluent color and dissolved organic carbon (DOC) are important control parameters. During this test, flowsheet dosages of virgin carbon (regenerated carbon not available at this date) reduced effluent DOC to 20 ppm (43 ppm goal) for the last seven days of the test and an average of 36 ppm for the entire test. Effluent color was 310 (540 goal) despite the feed color being 42% over design. The full scale, half-flow test results compare favorably with the PACT bench scale control. This table also presents insight into the improvement in effluent quality offered by PACT. Note the marked decrease in effluent DOC and color in the PACT full scale or bench scale units versus the biological bench scale unit.

In early May a full flowrate test was conducted. Table V presents operating conditions, feed and effluent quality for the test. The effluent color and dissolved organic carbon again met goals despite the feed color being 108% over design. Once again this test was conducted using virgin carbon.

In summary, this paper has presented an overview of some of the theoretical aspects of the combined powdered activated carbon-biological treatment process (PACT) and updated recent startup experiences from the 1.5×10^5 M^3/day installation based on this process at the Du Pont Chambers Works. This process is a versatile, viable wastewater treatment technology; we expect its use to become an accepted solution to a variety of existing and future wastewater treatment problems.

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5. Ferguson, J. F., G. F. P. Keoy, M. S. Merrill and A. H. Benedict "Powdered Activated Carbon - Biological Treatment: Low Detention Time Process" presented at the 31st Annual Purdue Industrial Waste Conference, West Lafayette, Indiana, May 4, 1976
6. Flynn, B. P. and L. T. Barry "Finding a Home for the Carbon: Aerator (Powdered) or Column (Granular)". Presented at the 31st Annual Purdue Industrial Waste Conference, West Lafayette, Indiana, May 1976
7. Flynn, B. P. "Operating Problem Solving During a Secondary-Tertiary Treatment Plant Start-Up". Presented at 11th Mid-Atlantic Regional ACS Meeting, University of Delaware, Newark, Delaware, April 22, 1977

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DISCUSSION

Ed Sebesta, Brown & Root: What is the design hydraulic loading for secondary clarifiers at the Chambers Works wastewater treatment facility?

Robertaccio and B. P. Flynn, Du Pont: The solid flux rate is designed at 250 lbs. per day per square foot which is kind of high. At that solid flux rate, you should be able to get an underflow concentration of 3-1/2 weight percent. In full scale testing we have been able to generate 7-1/2 weight percent solids which means we could operate without a waste sludge thickener and could feed our filter press directly from our return sludge line. The hydraulic overflow rate is in excess of about 1000 gallons/day/ft.^{2}. We have two secondary clarifiers but could send full flow through one secondary clarifier.

Leonard W. Crame, Texaco: What does the Du Pont PACT process patent mean to the refining industry in terms of using this process?

Robertaccio: Du Pont will license any user of the process. The royalty rate will be reasonable in order to encourage use of the process.

J. E. Rucker, API: Please comment on economics and feasibility of regeneration of powdered carbon from PACT sludge.

Robertaccio: Economics first. We think that powdered carbon can be regenerated for an operating cost of about 5¢ a pound. Capital costs would depend on the size of the facility and the method used to annualize capital costs. At Chambers Works capital costs would add another 5¢ a pound. Now feasibility. We put as much effort into the regeneration part of the Chambers Works facility as we did to the PACT process. The regeneration system is being brought on line. We have had some mechanical problems but we don't expect to have any more trouble solving these as we had solving other problems. Of course, a number of thermal and wet oxidation regeneration equipment manufacturers will tell you they think regeneration of powdered activated carbon from PACT sludge is no problem.

Dave Skamenca, Envirotech: Did you pilot test mixing the powdered activated carbon - biomass mixture with static mixers?

Robertaccio: Yes.

BIOGRAPHY Francis L. Robertaccio

Fran is a senior engineer for the DuPont Company in Wilmington, Delaware. He has 12 years experience in various industrial pollution control positions. He holds a B.S. and M.S. in Chemical Engineering from Clarkson College and a Ph.D. in Environmental Engineering from the University of Delaware. He has authored a dozen papers on industrial pollution control, holds several U.S. and foreign patents and is a member of AIChE and WPCF.

TABLE I - SYNERGISTIC EFFECT ON DOC REMOVAL WITH "PACT"

	DOC, mg/l			
TRIAL	FEED TO UNITS	BIO UNIT EFFLUENT	BIO UNIT EFFLUENT + BATCH CARBON ADSORPTION(1)	"PACT"(2) EFFLUENT
1	183	80	59	44
2	178	70	42	18
3	167	79	55	25

(1) Take 500 cc filtered Bio Unit effluent, add 150 ppm virgin carbon, stir 3 hours at room temperature, filter, and analyze filtrate for DOC

(2) "PACT" unit operating at 20°C with 8.0 day sludge age and 160 ppm carbon addition

TABLE II - REASONS TO CONSIDER PACT

I Existing Biological Treatment Plants
  A. Need to improve effluent quality
    - treatment plant hydraulically overloaded
    - biological treatment unstable
    - odor, foam
    - new, more restrictive effluent limits
    - biological treatment inherently incapable of removing some control parameters
    - water quality limitations not met in geographic area
  B. Need to reduce cost
    - rising sludge disposal costs
    - expensive chemicals used to aid biological treatment
  C. Need to expand treatment plant
    - want to accept new customers
    - currently overloaded
    - want to accept new product's wastewater; afraid biological process will become unstable or incapable of removing new waste constituents
    - can no longer use off plant sludge disposal site
  D. This treatment plant will eventually be abandoned (i. e., to join regional plant) but I have to get the most out of what I have

II New (potentially biological) Treatment Plants
  A. Want cost effective process
  B. Concern about efficiency of biological treatment
    - have potentially toxic waste
    - face strict effluent limits
    - want stable process
    - have wastewater from changing product line
    - future regulations might outdate biological treatment capabilities
  C. Have components in waste not currently regulated, but want them removed now.
  D. Limited amount of land available for treatment
  E. Want to minimize sludge disposal problems
    - have undesirable components in waste that will be concentrated in sludge; don't want these released to environment
    - don't have land, or availability of ocean disposal

III New Advanced Waste Treatment Plants
  A. Want cost effective process
  B. Want flexibility to alter treatment plant
    - as regulations change
    - as product mix dictates different treatment need -
      - over short intervals
      - over a long period
  C. Concerned about stability of alternate advanced treatment processes

D. Want to minimize investment

IV Miscellaneous

A. Pretreatment plus municipal disposal route too expensive

B. PACT is a low risk process compatible with many existing waste processing schemes, changes in product mix, or changes in regulations

TABLE III - ECONOMIC CONSIDERATIONS OF POWDERED ACTIVATED CARBON ADDITION

PRO	CON
• Eliminates granular carbon adsorption equipment needs, including initial GAC inventory	• Powdered Carbon Cost - virgin about 0.5-0.8¢/1000 liters/10ppm using 55 to 80¢/kg carbon • Regenerated (full cost) - about 0.1-0.2¢/1000 liters/10ppm
• Minimizes need for equalization facilities to control wastewater variability	
• Eliminates separate secondary sludge disposal if regeneration is used	
• Reduces or eliminates need for antifoam, odor control	• May require use of flocculant
• Protects biological system from inhibition or toxic upset	
• Reduces size requirements for secondary sludge settling, thickening, dewatering	
• Carbon addition rate readily changed for changes in wastewater characteristics or regulations	

TABLE IV - CHAMBERS WORKS HALF FULL FLOWRATE TEST TEST PERIOD 3/13/77-3/26/77 INCLUSIVE

	FULL SCALE PACT PLANT	BENCH SCALE CONTROLS	
		PACT	CONVENTIONAL BIOLOGICAL
Operating Conditions			
Carbon Dose(ppm)	182	150	0
Aeration Temp (°C)	22	22	22
Hydraulic Residence Time (hrs)	14.6	7.5	7.5
Sludge Age (days)	*	8	8
Feed Quality			
BOD-Soluble (mg/l)	304	304	304
DOC (mg/l)	214	214	214
Color (APHA)	1416	1416	1416
Effluent Quality			
BOD-Soluble (mg/l)	15.2	19.3	13.8
DOC (mg/l)	35.7	28.4	67.3
Color (APHA)	311	369	1900

*no steady state material balance available

TABLE V - CHAMBERS WORKS FULL FLOWRATE TEST TEST PERIOD 4/26/77-5/6/77 INCLUSIVE

Operating Conditions	
Carbon Dose (ppm)	189
Aeration Temp (°C)	28.5
Hydraulic Residence Time (hrs)	7.5
Feed Quality	
BOD - Soluble (mg/l)	300
DOC - (mg/l)	214
Color (APHA)	2080
Effluent Quality	
BOD - Soluble (mg/l)	9.6
DOC - (mg/l)	28
Color (APHA)	490

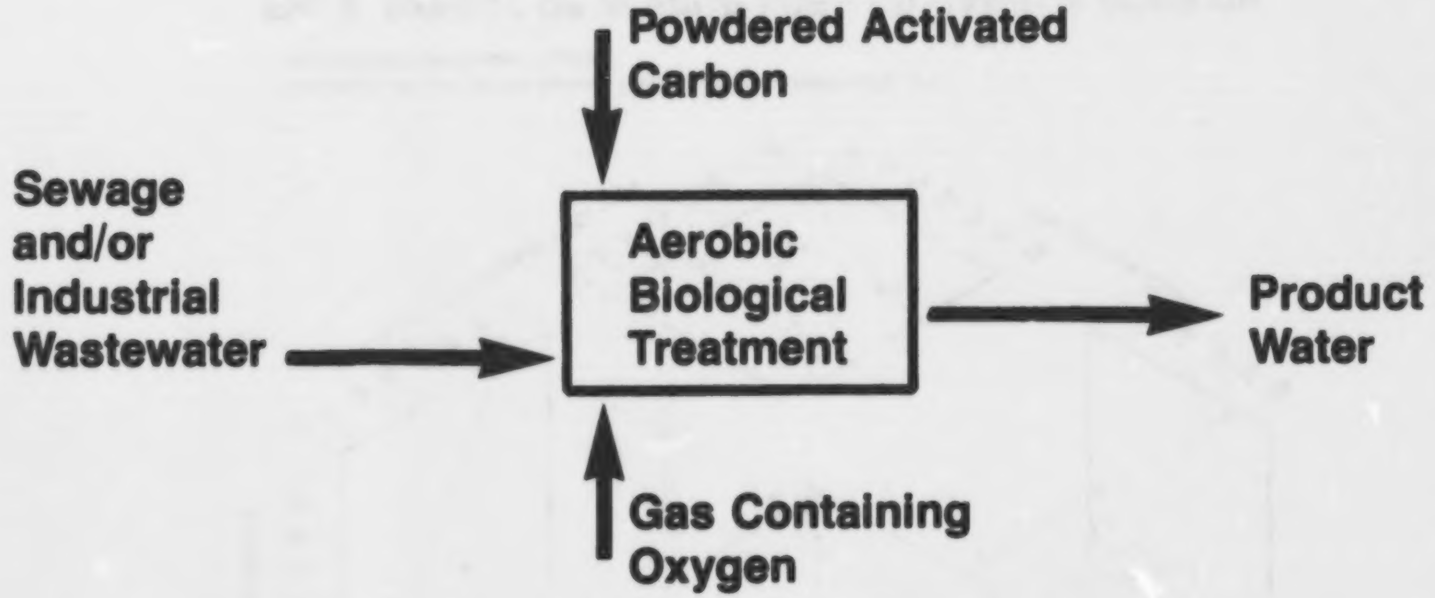
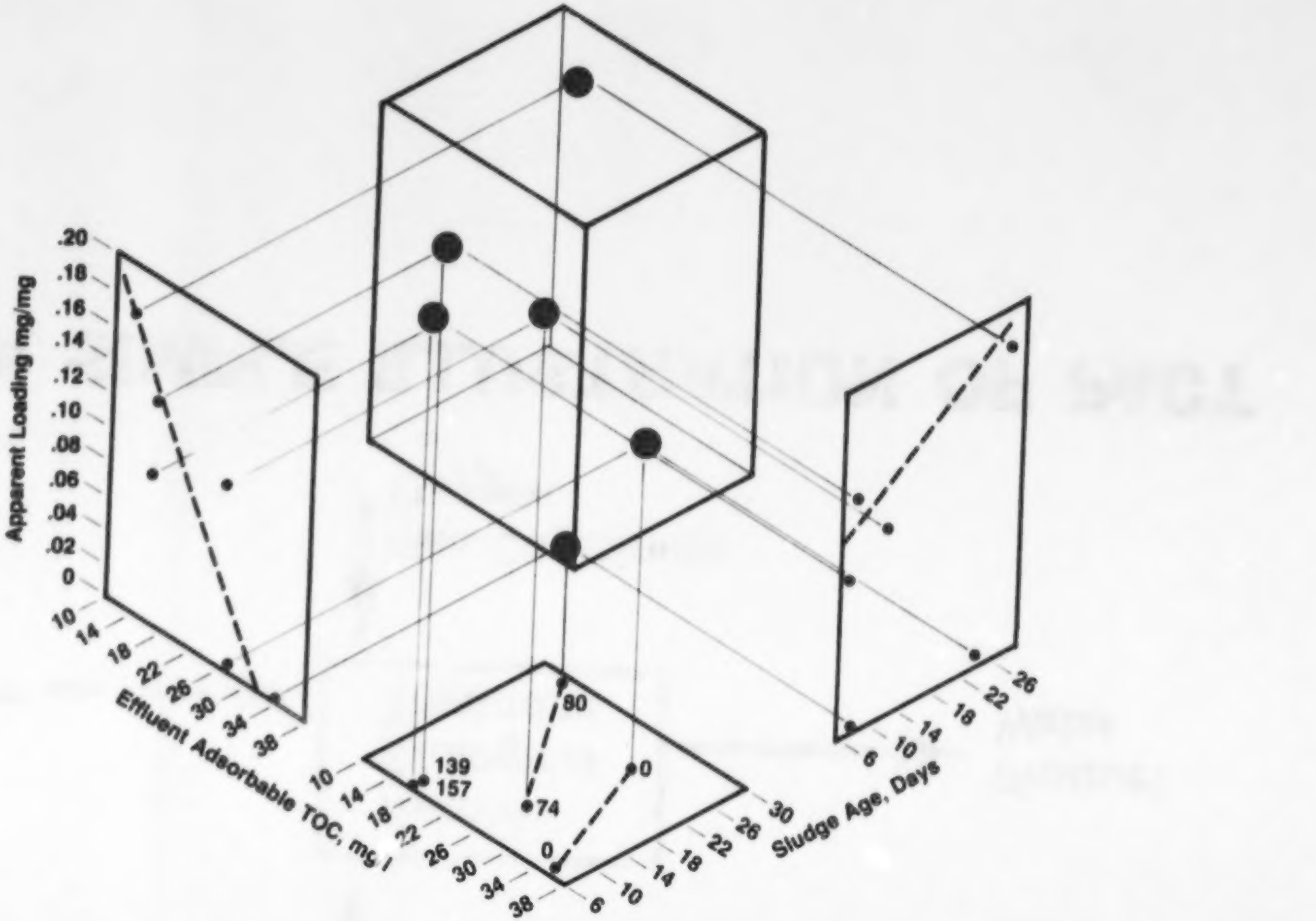
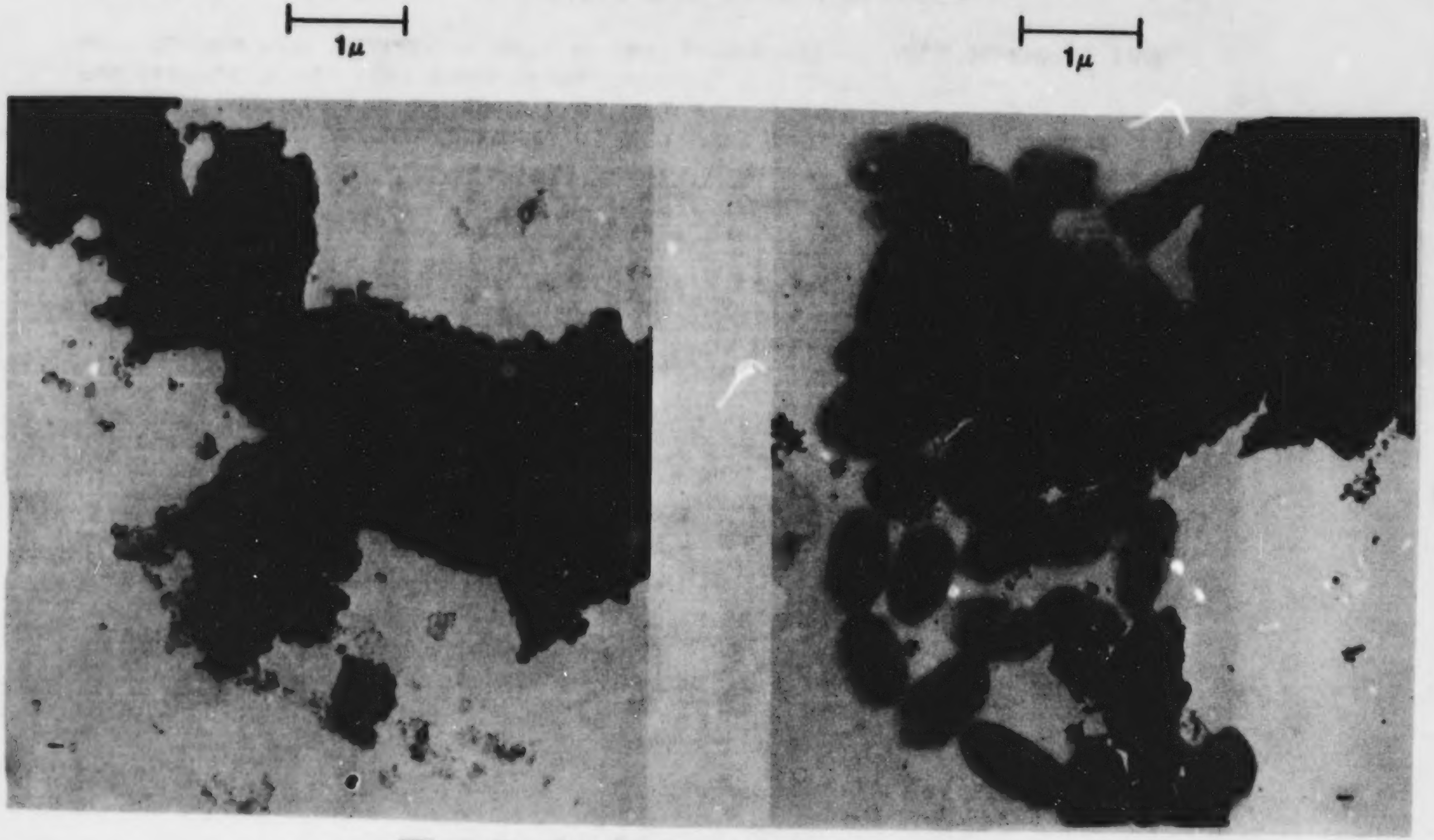

Powdered Activated Carbon
Sewage and/or Industrial Wastewater
Aerobic Biological Treatment
Product Water
Gas Containing Oxygen

Fig. 1 A SIMPLE ILLUSTRATION OF PACT



*Numbers shown in the bottom face of the exploded cube are applied carbon doses, mg/liter

Fig. 2 EFFECT OF SLUDGE AGE AND CARBON DOSE ON EFFLUENT TOC AND APPARENT LOADING



Left:

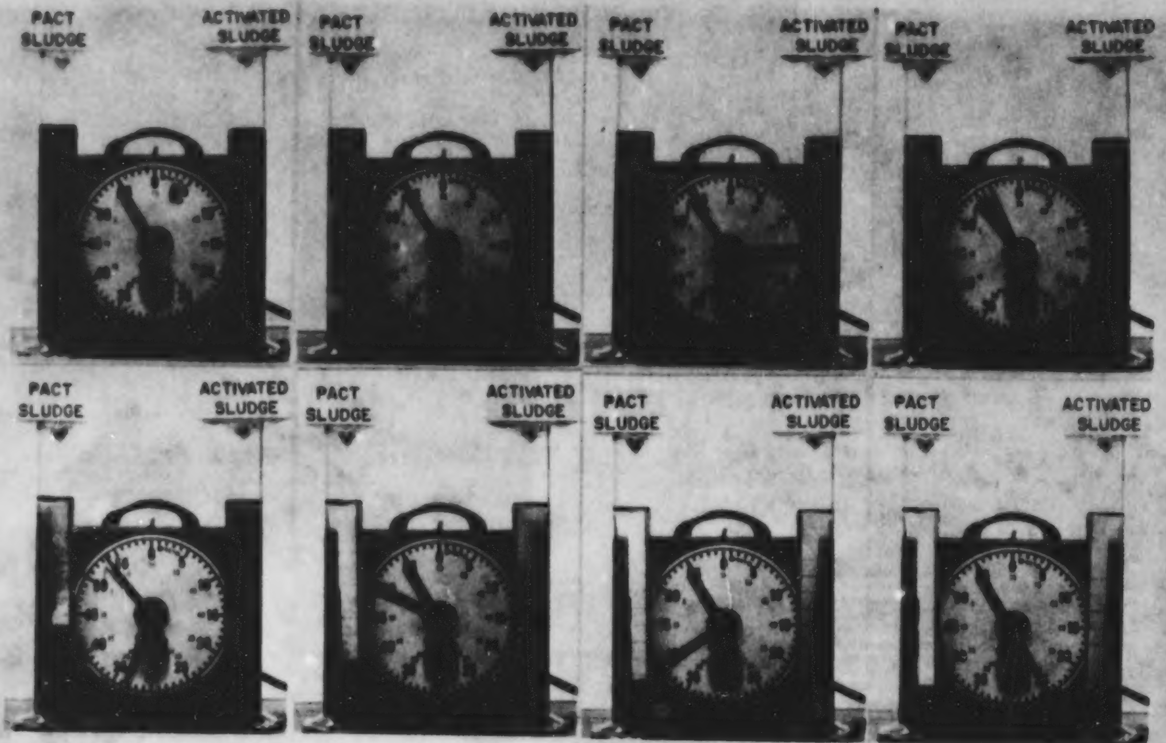
Virgin Carbon in Water

Right:

PACT Sludge

Fig. 3 PHOTOMICROGRAPHS

	INTIAL SOLIDS, MG/L	SLUDGE VOLUME INDEX, CC/GRAM
PACT	7708 ± 896	20 ± 2
ACTIVATED SLUDGE	2412 ± 150	46 ± 3



NOTE: TIMER HANDS MOVE COUNTERCLOCKWISE. READ ELAPSED TIME USING SMALL NUMBERS.
LONG HAND INDICATES MINUTES, SHORT HAND INDICATES SECONDS.
FOR EXAMPLE, LOWER LEFT TIMER READS 1 MINUTE, 21 SECONDS.
BOTH SLUDGES FROM TREATABILITY UNITS AT SAME SLUDGEAGE, HYDRAULIC DETENTION TIME.

Fig. 4 COMPARATIVE SETTLING CHARACTERISTICS OF PACT AND ACTIVATED SLUDGE

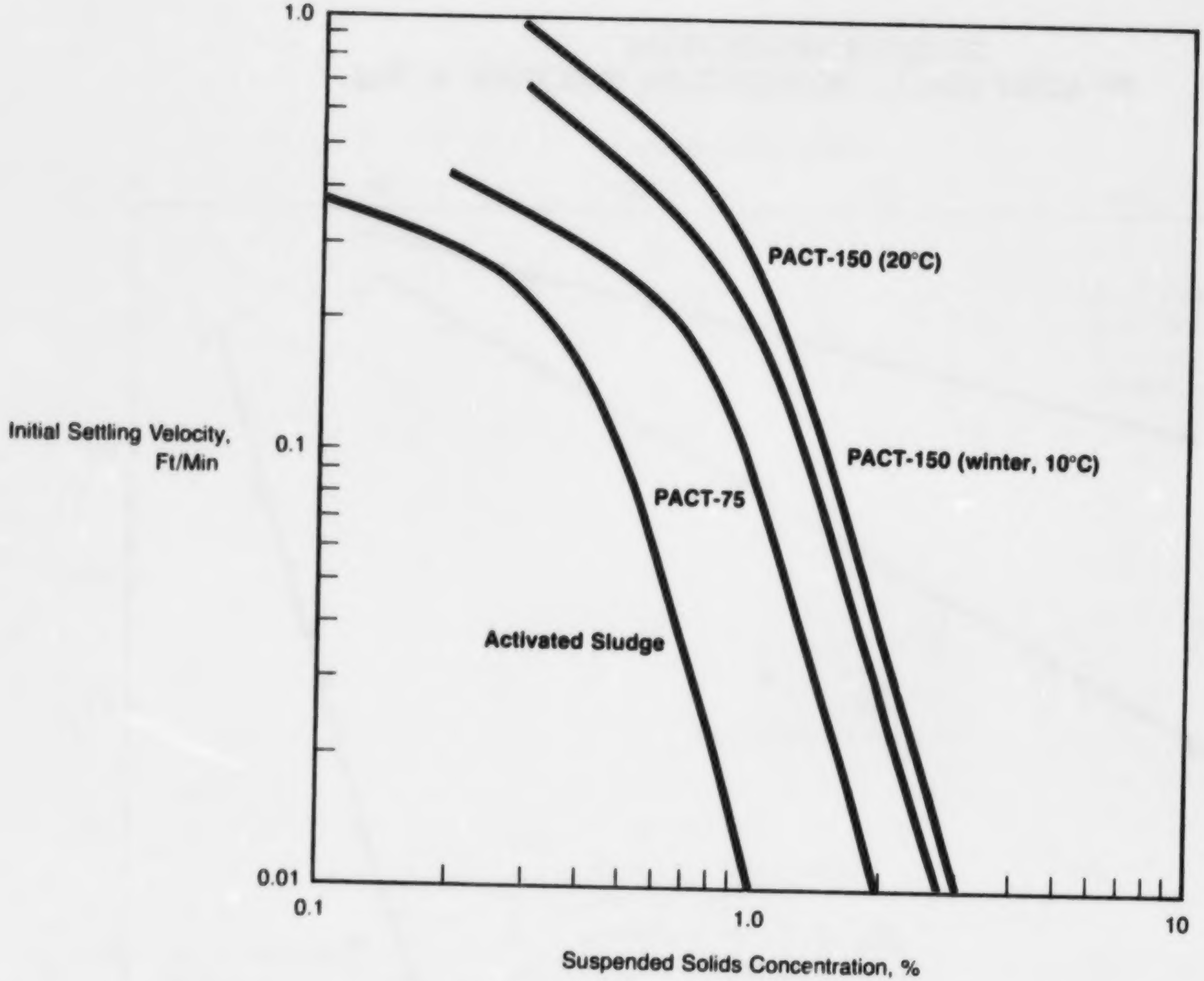


Fig. 5 SETTLING CHARACTERISTICS OF PACT & ACTIVATED SLUDGES

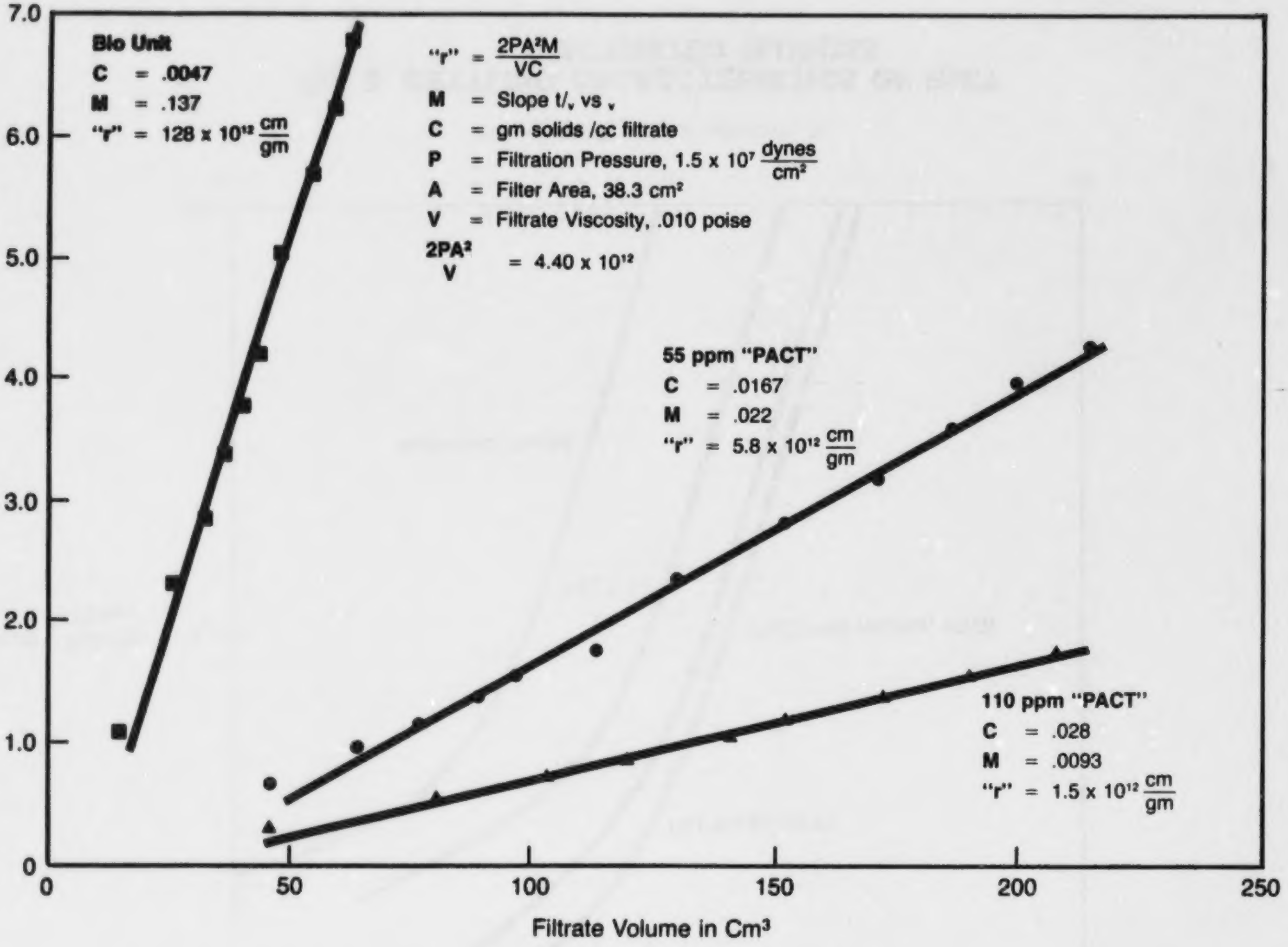


Fig. 6 SPECIFIC RESISTANCE, "r" OF PACT vs BIOLOGICAL SLUDGE

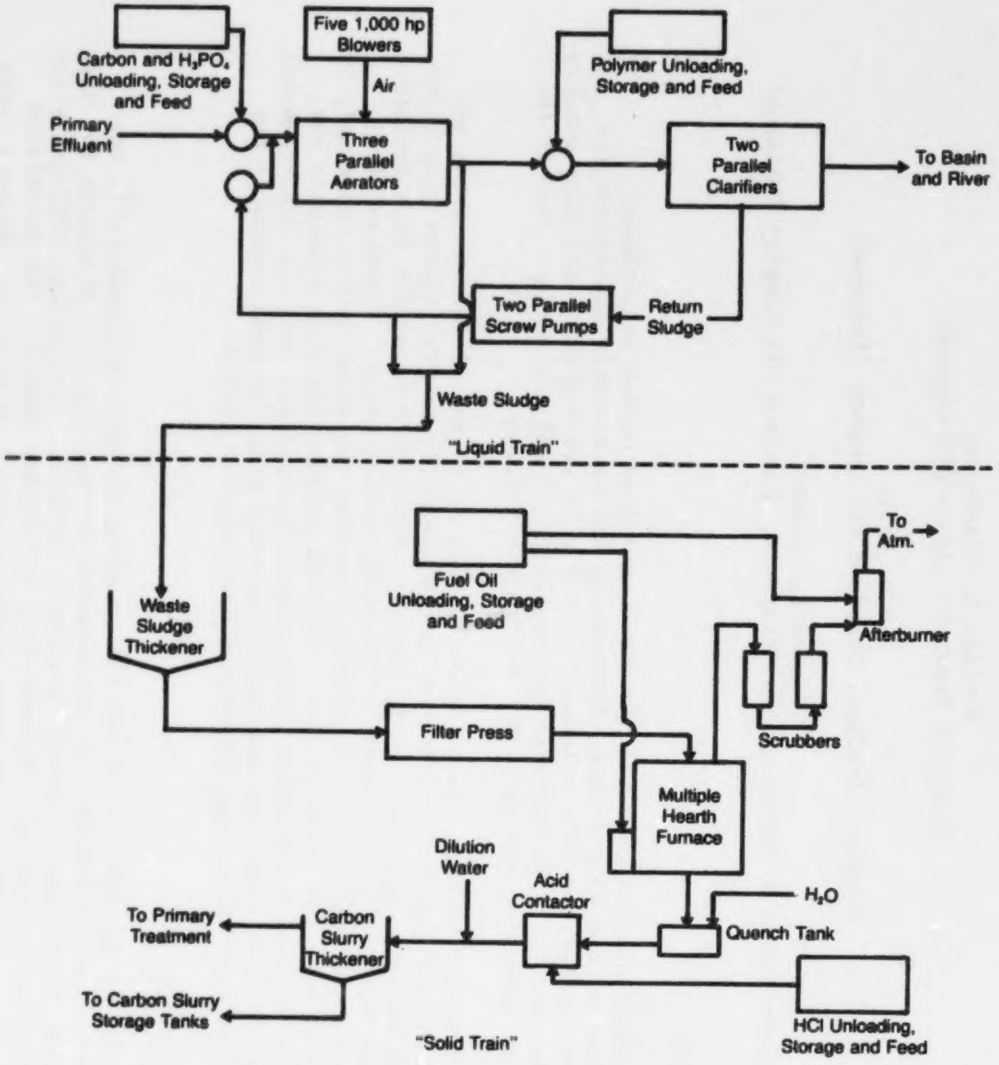


Fig. 7 DU PONT PACT PROCESS: CHAMBERS WORKS

POWDERED ACTIVATED CARBON ENHANCEMENT OF ACTIVATED SLUDGE FOR BATEA REFINERY WASTEWATER TREATMENT

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ABSTRACT

Pilot plant studies show that powdered activated carbon enhancement of activated sludge is a viable alternate to and less costly substitute for granular carbon tertiary treatment of refinery wastewaters. Effluent quality depends upon both the equilibrium concentration and the surface area of the powdered carbon in the activated sludge mixed-liquor.

Operation at very high sludge ages--60 days or more--allows the carbon to accumulate to high concentrations in the mixed-liquor even though only small make-up amounts are added to the system. Also, carbons with a high surface area are especially efficient in adsorbing contaminants. Consequently, costly regeneration may be unnecessary because the spent carbon can simply be discarded with the waste sludge. Powdered carbons may thus eliminate the need for the add-on granular carbon adsorption process that the Environmental Protection Agency has recommended for meeting proposed 1983 standards for Best Available Technology Economically Achievable (BATEA).

INTRODUCTION

According to the EPA guidelines for treating refinery wastewaters[1#], the sequence shown in Figure 1 is recommended for meeting 1977 standards for Best Practical Technology Currently Available (BPTCA). For meeting 1983 goals for Best Available Technology Economically Achievable (BATEA), the guidelines recommend an add-on process using granular carbon adsorption. However, this approach may be both inefficient and very costly. So far as is known, its effectiveness has never been adequately demonstrated. Moreover, preliminary estimates indicate that capital and operating costs for the granular carbon adsorption and regeneration facilities may equal or exceed those of the entire current activated sludge process.

By contrast, both patents and research studies[2-25] indicate that powdered activated carbon may be a practical and economical substitute for granular carbon. For example, powdered carbon costs only about one-half as much as

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[#] References inserted at end of text.

granular--\$0.65/kg versus \$1.20/kg[15]. In addition, recent studies have shown that powdered carbon can be added directly to the mixed-liquor in activated sludge aeration tanks [21, 22, 23, 24]. Thus, appropriate alterations in operating procedures may eliminate the need for regeneration by making it economically feasible to discard the spent carbon with the waste sludge.

In general, the cost effectiveness of a powdered carbon process increases with the concentration of carbon maintained in the mixed-liquor. A mass balance of such a process is represented by the following equation:

$$C = \frac{C_i \, \theta_c}{\theta_h} \qquad (1)$$

where

C = Equilibrium mixed-liquor carbon concentration (mg/l)
C_i = Influent carbon concentration (mg/l)
θ_c = Sludge age (days)
θ_h = Hydraulic retention time in the aeration tank (days)

Equation 1 reveals that the equilibrium mixed-liquor carbon concentration is proportional to the product of the influent carbon concentration (carbon dose) and the sludge age. Thus, equilibrium carbon concentration can be increased by increasing the carbon dose, or the sludge age, or both. Therefore, to keep carbon costs to a minimum, it is desirable to operate at as high a sludge age as possible and not at an excessively long hydraulic retention time.

A possible drawback to operation at a high sludge age is the increased risk that toxic, inhibitory, or inert materials will build up in the aeration tank. For example, a build-up of oily solids could reduce the oxygen transfer efficiency and inhibit both the nitrifying and organic carbon utilizing organisms. The dissolved oxygen concentration in the mixed-liquor could also become too low for effective nitrification, and the final clarifiers could become overloaded. Therefore, it is desirable in the pretreatment step to remove as much solid material as possible from the wastewater before it enters the aeration tank.

To evaluate the effects of such variables in a process using powdered carbon, an extensive 15 month four-phase pilot plant study was carried out at Amoco Oil Company's Texas City refinery. Pilot plants operating in parallel with the refinery activated sludge process facility were fed the same wastewater for treatment. Specific variables investigated were:

Carbon type, including surface area and pore volume

Carbon addition rate

Sludge Age

Pretreatment of feed to remove oil and solids

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EXPERIMENTAL EQUIPMENT

Figure 2 shows the configuration of the pilot plants. Each had a volume of 42 liters, and as many as eight units were operated in parallel during portions of the study. They were housed in a rain-tight enclosure but were neither heated nor cooled. Thus, the temperature of the mixed-liquor varied from 4°C to 31°C.

Operating conditions and analytical procedures are summarized in Table 1. The pH was checked daily and controlled by addition of caustic at a constant rate. Dibasic potassium phosphate, K_2HPO_4, was added to satisy the phosphorus requirement of the microorganisms.

The wastewater feed, a slipstream from the pressure filters of the refinery treatment plant, was passed through a pilot gravity sand filter before being fed to the pilot plants.

Table 2 summarizes the characteristics of the five powdered carbons evaluated. Amoco's experimental high-surface-area carbons are designated as A1 and A2, PX-21 and PX-23, respectively. Those designated as B, C, and D are commercially available carbons having a much lower surface area. Carbon A2 (PX-23) has the highest pore volume.

Effectiveness was judged on the basis of the following effluent standards proposed for a BATEA facility[1]:

	Concentration, mg/liter
Total Organic Carbon (TOC)	15
Chemical Oxygen Demand (COD)	24
Ammonia (NH_3-N)	6.3
Phenolics	0.02

These standards are for a Class "C" refinery and are based on the guideline effluent flow rate of 0.46 m^3/m^3 of crude throughput per stream day (19 gal/bbl). Because the BATEA treatment sequence will undoubtedly result in very low concentrations of effluent suspended solids, only the soluble components of the effluent were measured.

To obtain high sludge ages, effluent suspended solids were allowed to settle in 30-gallon plastic containers and then were returned to the pilot plants periodically. At any given sludge age, all plants were allowed to reach steady-state operation over an extended period of time. Then performance data were taken over a 30-day period.

RESULTS AND DISCUSSION

The four phases of the study were carried out in sequence, with the design of succeeding phases based on the results of the preceding ones. In summary, they examined:

Phase	Objective
I	Effect of carbon type at an addition rate of 100 mg/liter and a sludge age of 20 days with prefiltered feed.
II	Effect of carbon type at an addition rate of 200 mg/liter and a sludge age of 20 days with prefiltered feed.
III	Effect of increasing sludge age to 60 days and reducing carbon addition rate to 25 mg/liter with unfiltered and prefiltered feed.
IV	Effect of further increasing sludge age to 150 days while reducing carbon addition rate to 10 mg/liter.

Phases I and II

The results of Phases I and II, summarized in Table 3, indicate that powdered activated carbon significantly enhances the performance of a refinery activated sludge process. Improvement in the quality of the effluents from carbon-fed plants ranged from 65% for soluble organic carbon up to 95% for phenolics. At the 200 mg/liter addition rate, the results usually satisfied the BATEA effluent quality goals. The high surface area carbon A1 was significantly more effective than the other three. The commercially available carbon B produced slightly better effluent than carbon C, which would be expected if efficiency is proportional to surface area. Because nitrification was essentially complete in the control unit, carbon addition could not improve ammonia conversion. Carbon D, which is derived from wood charcoal and has a significantly lower pore volume than the others, performed so poorly in Phase I that it was dropped from further consideration. The performance of carbon A1 at 100 mg/liter dose was about as effective as carbon B at 200 mg/liter, or about twice as effective as the best commercially available carbon tested.

Phase III

Table 4 shows the effects of sludge age and feed filtration upon performance. The plant with filtered feed performed better than one with unfiltered feed, and a sludge age of 60 days was better than one of 20 days. No deterioration in the settling characteristics of the mixed-liquor suspended solids was observed at this higher sludge age.

At a sludge age of 20 days the plant with filtered feed performed marginally better than the one with unfiltered feed. Undoubtedly, greater differences in effluent quality would have been observed in a plant operated at a sludge age of 60 days with unfiltered feed. (Not recorded in these data, however, is the complete failure of the plant fed unfiltered feed shortly after cessation of data gathering for this steady-state period.)

Table 4 also shows how pore size and surface area affect the performance of the carbons. Carbons A1 and A2 have approximately the same surface area, but carbon A2 has much larger pores. Yet, at an equivalent addition rate of 50 mg/liter, both carbons showed about the same performance. Thus, large pore diameters are not required for effective treatment of this refinery wastewater. Moreover, plants fed 50 mg/liter of either A1 or A2 performed much better than the plant fed 100 mg/liter of carbon B. In fact, these high-surface-area carbons are between two and four times more effective than carbon B in enhancing SOC and soluble COD removal.

A comparison of the data in Tables 3 and 4 shows that a low carbon dose and a high sludge age enhance an activated sludge process almost as much as do a high carbon dose and a low sludge age.

It is possible that the difference in performance is solely due to difference in temperature between the phases--mean operating temperature during Phase III was only 14°C, whereas during Phases I and II temperature averaged 31°C and 25°C, respectively.

Also observed during the lower operating temperature of Phase III was an increase in the ammonia removal efficiency of the carbon-fed pilot plants. This phenomenon was unexpected because activated carbon does not normally adsorb ammonia. Possibly, the increased removal rate is due to the adsorption of potentially toxic or inhibitory organic materials which would reduce the rate of nitrification if left in solution. The control plant in Phases I and II had little difficulty in achieving full nitrification, perhaps because of the higher temperature.

Phase IV

As shown in Table 5, Phase IV was designed to push the activated sludge system to the limit by increasing sludge age to 150 days and decreasing carbon addition to 10 mg/liter. Further, in one of the plants, hydraulic retention time was reduced to 7.5 hours, compared with 15 hours in the other plants.

Despite similarities in influent quality during all four phases, during Phase IV the effluent SOC and COD of the control increased by about 30-35% over that observed during the first three phases, despite a mean temperature of 27°C (c.f. 14°C during Phase III). All pilot plants essentially nitrified completely.

Remarkably, however, the plant with 10 mg/liter of high surface area carbon A1 at a sludge age of 150 days produced an effluent whose soluble organic carbon concentration was 50% lower than that of the control reactor and slightly lower than that of all of the other pilot plants. The plant dosed with 25 mg/liter carbon A1, with one-half the hydraulic capacity of the other plants, produced the second best effluent.

The outstanding performance at a sludge age of 150 days indicates that refinery activated sludge processes can be operated with very little added carbon. The dose may be low enough so that the carbon need not be regenerated but be discarded with the waste activated sludge. At a very high sludge age, there will be smaller quantities of waste sludge to be disposed of.

The data in Table 5 also indicates that powdered carbon can be used to increase the hydraulic capacity of an activated sludge plant, as proposed by others[13], or to increase the effluent quality of an overloaded plant. The carbon-fed plant that operated at one-half the hydraulic retention time of the control produced an effluent 50% better than that of the control. Experience with pilot activated sludge plants operated at several of Amoco's other refineries has shown that conventional activated sludge processes cannot be operated successfully with a hydraulic residence time of only 7½ hours.

Status of Powdered Carbon Enhancement of Activated Sludge

The data from Phase IV indicate that the limits of the powdered carbon enhanced activated sludge process have not been reached. In addition, more data are needed before economic studies can be made to weigh the possible options for achieving a given effluent quality: high fresh carbon dose at moderate sludge age (20-60 days) with regeneration of spent carbon; low fresh carbon dose at high sludge age (60-150 days) with no regeneration of spent carbon. Cost analyses should be made for each of these extreme options, and several intermediate ones, and compared with those for tertiary treatment with granular carbon technology.

Figure 3 shows the qualitative curves this pilot study has generated. Of course, the one for the 150-day sludge age is purely speculative because only one data point exists. However, the trend of the data does show that effluent quality is a function of mixed-liquor carbon concentration. The curves are probably asymptotic to a residual organic carbon concentration, but over the range investigated an increase in mixed-liquor carbon concentration causes a decrease in effluent soluble organic carbon. Furthermore, the relationship between effluent quality, sludge age, and carbon dose is clearly non-linear. For example, to achieve an effluent quality of 12.5 mg/liter of soluble organic carbon, the three options are: 100 mg/liter of carbon at a sludge age of 20 days; 47 mg/liter of carbon at a sludge age of 60 days; 24 mg/liter of carbon at a sludge age of 150 days. If the relationship were linear, the values calculated from a base case of 100 mg/liter at a 20-day sludge age would be 33 mg/liter and 13 mg/liter at 60 days and 150 days, respectively.

Apparently, the process loses effectiveness because of incomplete microbial regeneration. Microbial regeneration of the spent carbon is probably not as effective as using fresh carbon; some materials adsorbed by the carbon are undoubtedly non-biodegradable, even after 150 days of contact with microorganisms in the pilot plant. The ability to retain significant effectiveness even at 150 days is the key to cost effective high sludge age operation with powdered activated carbon. Of course, there may be other reasons why carbon loses effectiveness at high sludge age, such as production of cell lysis products which are then adsorbed by the carbon.

Effluent Variability

Variation in effluent quality over a 30-day (or longer) period is extremely important. The EPA[1] has set the daily maximum variability equivalent to the 99% probability value and the 30-day maximum variability to the 98% level. For BATEA the daily maximum variability factors for TOC, COD, NH_3-N, and phenolics are proposed at 1.6, 2.0, 2.0, and 2.4, respectively. The 30-day maximum values are 1.3, 1.6, 1.5, and 1.7, respectively.

Figures 4, 5, 6, and 7 show probability data for the 30-day operating periods during Phase III. Table 6 shows the daily maximum (99% probability) and 30-day maximum (98% probability) variability factors calculated from these figures for the plant fed with 25 mg/liter of Carbon A1. The EPA guideline values are also given. The actual variability factor was calculated as the 99% (or 98%) probability value divided by the target quality value. In general, the variability in effluent quality was higher than the guideline values.

It is important to note that the proposed guideline variability factors are unrealistic. The data base used by EPA[1] for their production was obtained from limited pilot studies. In addition, BPTCA 30-day maximum (98% probability) values were used as the BATEA 30-day maximum values. Variability factors will undoubtedly have to be amended before BATEA goals become BATEA standards.

SUMMARY AND CONCLUSIONS

A viable alternative to granular activated carbon tertiary treatment of refinery activated sludge effluent for meeting proposed 1983 BATEA effluent quality standards has been demonstrated. The proposed process involves adding powdered activated carbon to the aeration tank of the activated sludge process, achieving cost effectiveness by operating at a very high sludge age and a low carbon dose. Effective removal of oil and colloidal solids in the pretreatment step is necessary for successful operation.

Effluent quality depends upon both the equilibrium mixed-liquor carbon concentration and the surface area of the carbon. An experimental carbon with a high surface area appears to be several times more effective than the best commercial carbons in achieving an effluent quality standard. Pore size of the activated carbon had no apparent effect upon effluent quality.

In general, the process can be used to meet only the long-term average effluent quality proposed for BATEA. Daily maximum and 30-day maximum variability goals, as presently defined cannot be met.

The proposed process also enhances nitrification at low temperatures and dampens effects of increased hydraulic flow rate on the activated sludge factors. Both phenomena will help to decrease effluent variability.

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DISCUSSION

Piysuch Shah, Exxon Research and Engineering Co.: Would you please comment on the effects of toxicant build up and on the performance of aged activated sludge units, especially 100-150 days? Also, what is the maximum concentration that can be allowed in the feed?

Grieves: Assume a very high sludge age of 150 days, a hydraulic residence time of 12 hours, 1 mg/liter of a toxicant (for example, chromium) in the feed, and 100% removal of it by the activated sludge. At steady state, chromium concentration would build up to 300 mg/liter, which, in all likelihood, would be toxic to the microorganisms. However, we have data to indicate that even at 150 days sludge age, chromium does not accumulate to more than 30-50 mg/liter in the sludge. We certainly have not observed any effects of toxicant build-up -- on the contrary, the 150-day sludge age reactor is the most effective unit.

As for other toxicants -- for example oil and grease and inert suspended solids -- if they are not effectively removed by prefiltration, or air flotation, they could very well accumulate to toxic or inhibitory concentrations in the mixed-liquor. As well as being toxic or inhibitory to microorganisms, especially nitrifiers, oxygen transfer problems will be encountered. High inert solids concentrations may also cause overloading problems in the final clarifier.

Ed Sebesta, Brown & Root, Inc.: The data indicates that nitrification occurred during some phases of the experiments while nitrification did not occur during other phases. Do you have any comments about why this occurred?

Grieves: If you have ever operated a refinery wastewater treatment facility, you will know that frequently there are excursions with nitrification. We achieved good nitrification during the warm operating periods, phases I and II. During phase III operation, it was relatively cool -- we recorded a mixed-liquor temperature of 2°C on one occasion, quite a severe winter for this part of Texas -- and, as expected, nitrification in the control activated sludge plant was poor. This is reflected in the probability plot (Figure 6) of the data. However, in the activated sludge pilot plants to which carbon was added, almost complete nitrification was observed. This was unexpected because, as you know, carbon does not normally adsorb ammonia.

Bob Smith, Carborundum Co.: Have you compared the cost effectiveness of the high capacity Amoco carbon vs. the lower capacity carbons?

Grieves: No, we have not made this comparison yet. We have not decided whether to go commercial with our carbon or not. However, if and when we do decide to commercialize our product, you can rest assured that it will be cost effective with other commercially available carbons.

BIOGRAPHIES

Colin G. Grieves is a Research Engineer in the Water Conservation group at Amoco Oil Company's Research and Development department in Naperville Illinois. He has M.S. and Ph.D. degrees in Environmental Systems Engineering from Clemson University, Clemson, South Carolina, and a B.Sc. degree in Civil Engineering from the University of Newcastle Upon Tyne, England. Previous employment was in the Public Health Engineering Division of Babtie Shaw & Morton, Consulting Civil and Structural Engineering in Glasgow, Scotland. Colin is the author of several papers in the wastewater treatment field.

Michael K. Stenstrom is a Research Engineer in the Water Conservation group at Amoco Oil Company's Research and Development department in Naperville, Illinois. He has a B.S. degree in Electrical Engineering and M.S. and Ph.D. degrees in Environmental Systems Engineering from Clemson University, Clemson, South Carolina. Mike is the author of several papers dealing with various aspects of municipal and industrial wastewater treatment.

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BIOGRAPHIES

Joe D. Walk is Active Carbon Project Director in the Corporate Development Department of Standard Oil (Indiana), Chicago, Illinois. He has a B.S. degree in Chemical Engineering from the University of Texas. Previously he served as Process Coordinator in air/water conservation, crude running and product treating for Amoco Oil's ten refineries. Prior assignments include Manager of Technical department at Texas City refinery, as well as positions in New York City, New Orleans, and El Dorado, Arkansas, during his 31 years service with Standard Oil.

James F. Grutsch is Coordinator-Environmental Projects, Standard Oil Company (Indiana). He holds undergraduate and graduate degrees in chemistry from Indiana University. Prior to his present assignment with Standard, Jim served successfully as Group Leader for finishing, blending and reclamation at the Amoco Oil Whiting refinery, and Coordinator of Waste Disposal for Amoco. Jim taught undergraduate chemistry for 6 years at Indiana.

TABLE 1 OPERATING CONDITIONS

Pilot Plant Conditions

Aeration Zone Volume	36.7	liters
Settling Zone Volume	5.7	liters
Nominal Flow Rate	2.45	liters/hr.
Nominal Hydraulic Retention Time	15.0	hours
Nominal Settling Time	2.33	hours
Air Flow Rate	300	liters/hr.
pH	6-8.5	
Caustic Addition Rate	0.12-0.30	liters/hr.
Phosphorous Added to Feed	3	mg/liter
Temperature	Ambient (4-31°C)	

Analytical Work

Frequency	Analysis Performed[27, 28]
Daily	Influent and mixed-liquor pH, temperature, influent flow rate, caustic addition rate. Carbon addition and sludge wastage.
3 Times a Week	Influent and effluent total and volatile suspended solids, soluble organic carbon, soluble chemical oxygen demand, soluble ammonia nitrogen, and soluble phenolics. Mixed-liquor suspended solids and mixed-liquor volatile suspended solids. Sludge volume index.
Once a Week	Material balances to calculate quantity of sludge to be wasted to maintain desired sludge age.

TABLE 2 PROPERTIES OF POWDERED ACTIVATED CARBONS

Property	Carbon Designation				
	Experimental Amoco High Surface Area -		Commercially Available Conventional Surface Area Carbons		
	A1	A2	B	C	D
	Grade PX-21	Grade PX-23			
Surface Area BET, m^2/g	3099	3148	717	514	532
Pore Volume, cc/g					
> 15 A° Radius	0.16	0.43	0.28	0.38	0.03
< 15 A° Radius	1.45	1.60	0.51	0.11-0.42	0.25
Iodine Number	3349	3375	1790	920	888
Methylene Blue Adsorption, mg/g	586	550	100	83	50
Phenol Number	12.8	12.6	34.1	22.9	23.8
Bulk Density, g/cc	0.298	0.228	0.610	0.576	0.484
Screen Analysis					
Passes 100 Mesh, Wt.%	98.4	99.1	99.2	100.0	100.0
Passes 200 Mesh, Wt.%	92.7	93.4	86.7	94.4	97.9
Passes 325 Mesh, Wt.%	84.1	80.8	60.6	68.3	91.8
Molasses Number	10	205	103	85	0

TABLE 3

PHASES I AND II - EFFECT OF CARBON TYPE AND ADDITION RATE ON EFFLUENT QUALITY*
50% Probability Data During 30 Days of Steady-State Operation
Sludge Age = 20 Days

	Concentration, mg/liter					
		Pilot Plant Effluent				
Component	Filtered Influent	No Carbon	Carbon A1	Carbon B	Carbon C	Carbon D
Phase I: Carbon Addition Rate = 100 mg/liter Equil. Mixed-Liquor Temp = 31°C, Carbon Conc = 3200 mg/liter						
SOC	72.0	22.0	12.5	17.5	18.5	23.0
SCOD	230	73	28.5	48	44	65
NH_3-N	25.8	0.5	0.2	0.5	0.5	0.5
Phenolics	4.35	0.018	0.003	0.010	0.010	0.017
Phase II: Carbon Addition Rate = 200 mg/liter Equil. Mixed-Liquor Temp = 25°C, Carbon Conc = 6400 mg/liter						
SOC	70.0	26.5	9	13.5	15.5	
COD	230	58	17	24	28	
NH_3-N	25.4	0.2	0.2	0.2	0.1	
Phenolics	4.06	0.020	0.001	0.001	0.003	

* BATEA effluent standards in mg/liter are:

Soluble Organic Carbon (SOC)	15
Soluble COD (SCOD)	24
Ammonia Nitrogen (NH_3-N)	6.3
Phenolics	0.02

TABLE 4

PHASE III - EFFECT OF CARBON TYPE AND ADDITION RATE, SLUDGE AGE, AND INFLUENT PRETREATMENT ON EFFLUENT QUALITY

50% Probability Data During 30 Days of Steady-State Operation
Equil. Mixed-Liquor Temp = 14°C, Carbon Conc. = 2400 mg/liter

	Carbon		Influent Concentration, mg/liter			
Influent Pretreatment	Type	Addition Rate, mg/liter	SOC	COD	NH_3-N	Phenolics
Filtered Feed	-	-	73.5	294.5	19.3	3.95
			Effluent Concentration, mg/liter			
		Sludge Age = 20 Days				
Unfiltered	-	-	32.0	103.5	12.1	0.027
Filtered	-	-	29.0	83.0	14.5	0.027
		Sludge Age = 60 Days				
Filtered	-	-	25.0	65.9	5.1	0.019
Filtered	B	100	16.0	40.3	0.2	0.001
Filtered	A1	50	12.0	27.5	0.1	0.002
Filtered	A1	25	16.0	50.3	0.4	0.006
Filtered	A2	50	13.0	31.0	1.8	0.004

TABLE 5

PHASE IV - EFFECT OF HIGH SLUDGE AGE, LOW CARBON ADDITION RATE, AND DECREASED HYDRAULIC RETENTION TIME ON EFFLUENT QUALITY*

50% Probability Data During 30 Days of Steady-State Operation
Equil. Mixed-Liquor Temp = 27°C

Carbon		Sludge Age, days	Hydraulic Retention Time, hr	Equil. Mixed Liquor Carbon Conc, mg/liter	Effluent Conc, mg/liter			
Type	Addition Rate, mg/liter				SOC	COD	NH_3-N	Phenolics
-	-	60	15	-	29	99	0.1	0.018
B	25	60	15	2400	22	64	0.1	0.010
Al	25	60	15	2400	18	52	0.1	0.010
Al	25	60	7.5	4800	17	46	0.3	0.010
Al	10	150	15	2400	16	49	0.1	0.010

* Filtered influent contained 78 mg/liter SOC, 270 mg/liter COD, 29 mg/liter NH_3-N, and 3.25 mg/liter phenolics.

TABLE 6

PHASE III - BAT GUIDELINE AND ACTUAL VARIABILITY FACTORS FOR PILOT PLANT FED 25 mg/liter OF CARBON A1

Parameter	BAT Guideline Variability Factor		Actual Variability Factor	
	Daily Max.	30 Day Max.	Daily Max.	30 Day Max.
Soluble Organic Carbon	1.6	1.3	2.8	2.8
Soluble COD	2.0	1.6	7.5	7.5
NH_3-N	2.0	1.5	2.1	2.0
Phenolics	2.4	1.7	5	5

FIGURE 1. SIMPLIFIED REFINERY BPT WASTEWATER TREATMENT SYSTEM

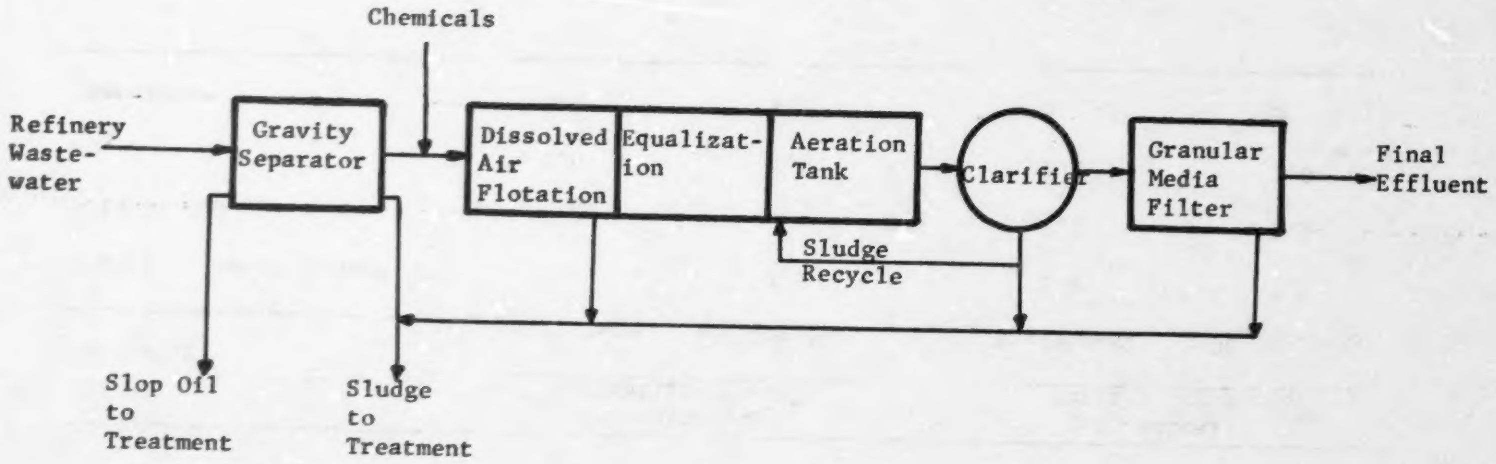


FIGURE 2. SCHEMATIC OF ACTIVATED SLUDGE REACTOR USED IN PILOT PROGRAM

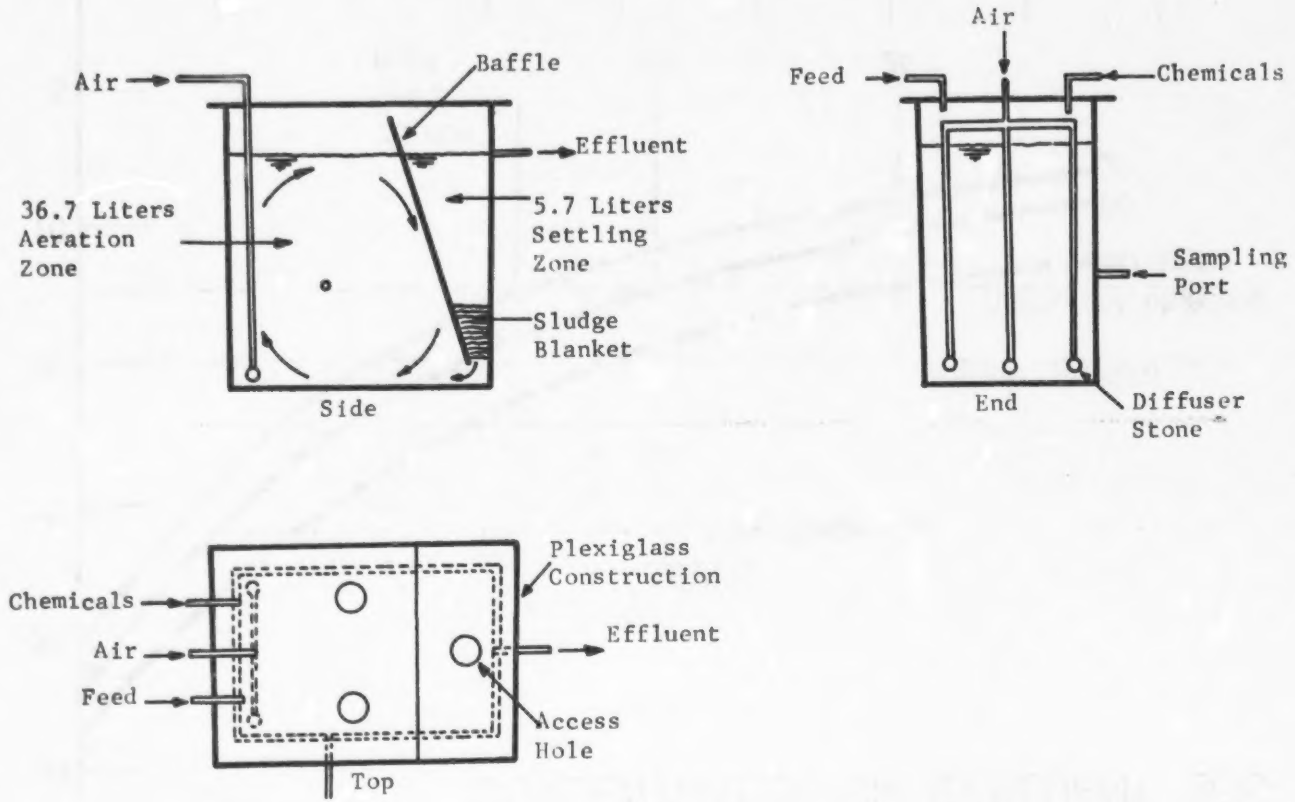
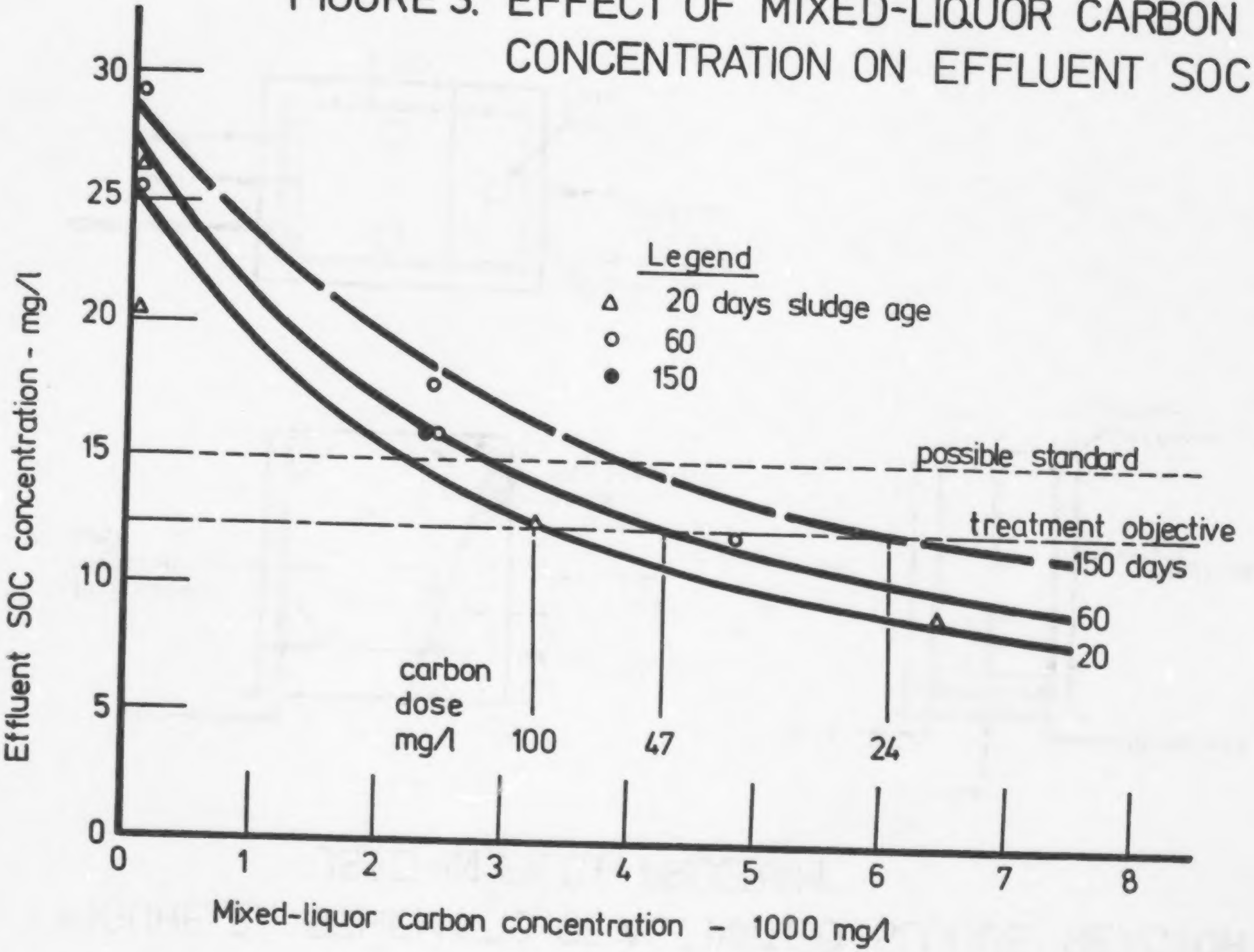


FIGURE 3. EFFECT OF MIXED-LIQUOR CARBON CONCENTRATION ON EFFLUENT SOC



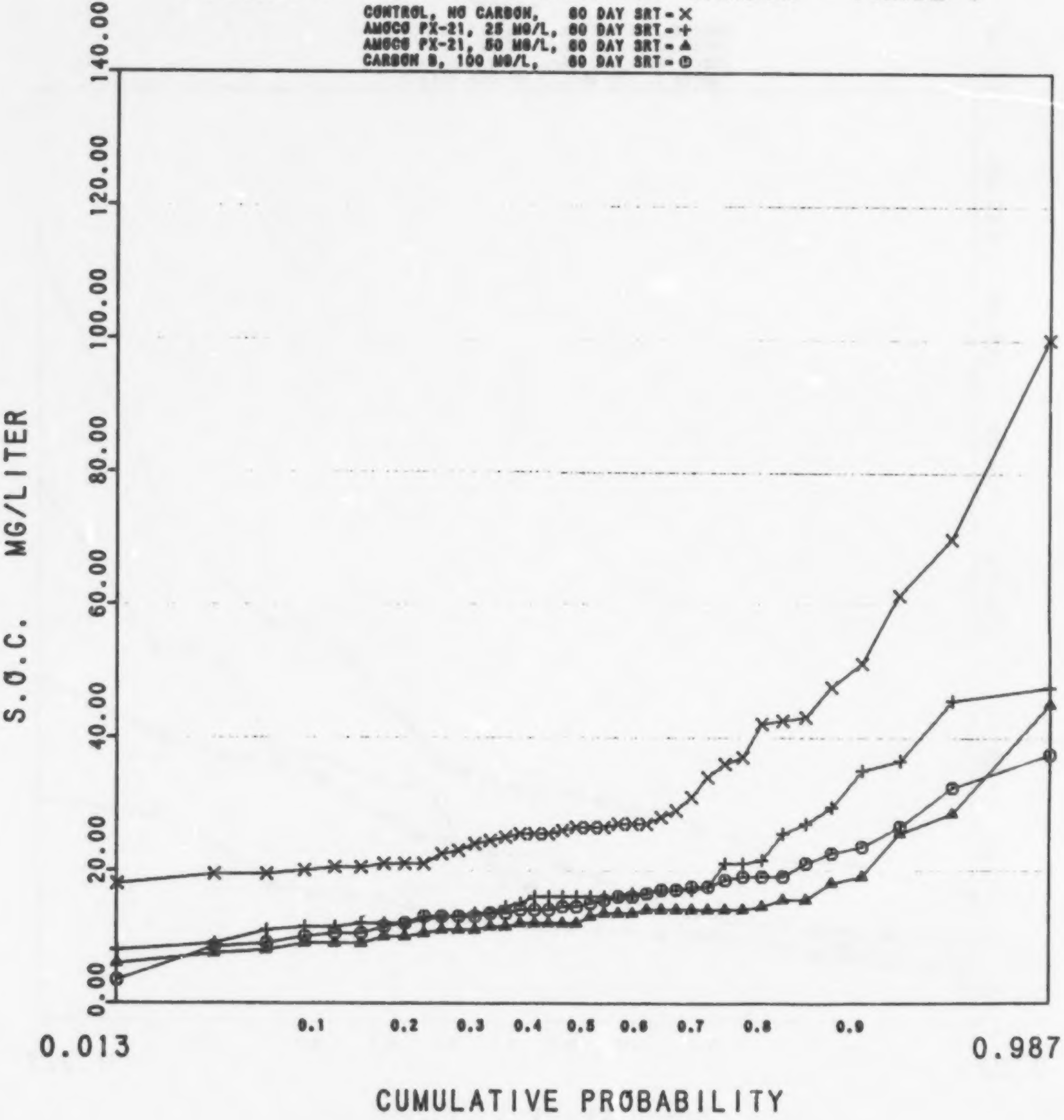


FIGURE 4 - SOLUBLE ORGANIC CARBON - PHASE 3

FIGURE 5 - SOLUBLE CHEMICAL OXYGEN DEMAND

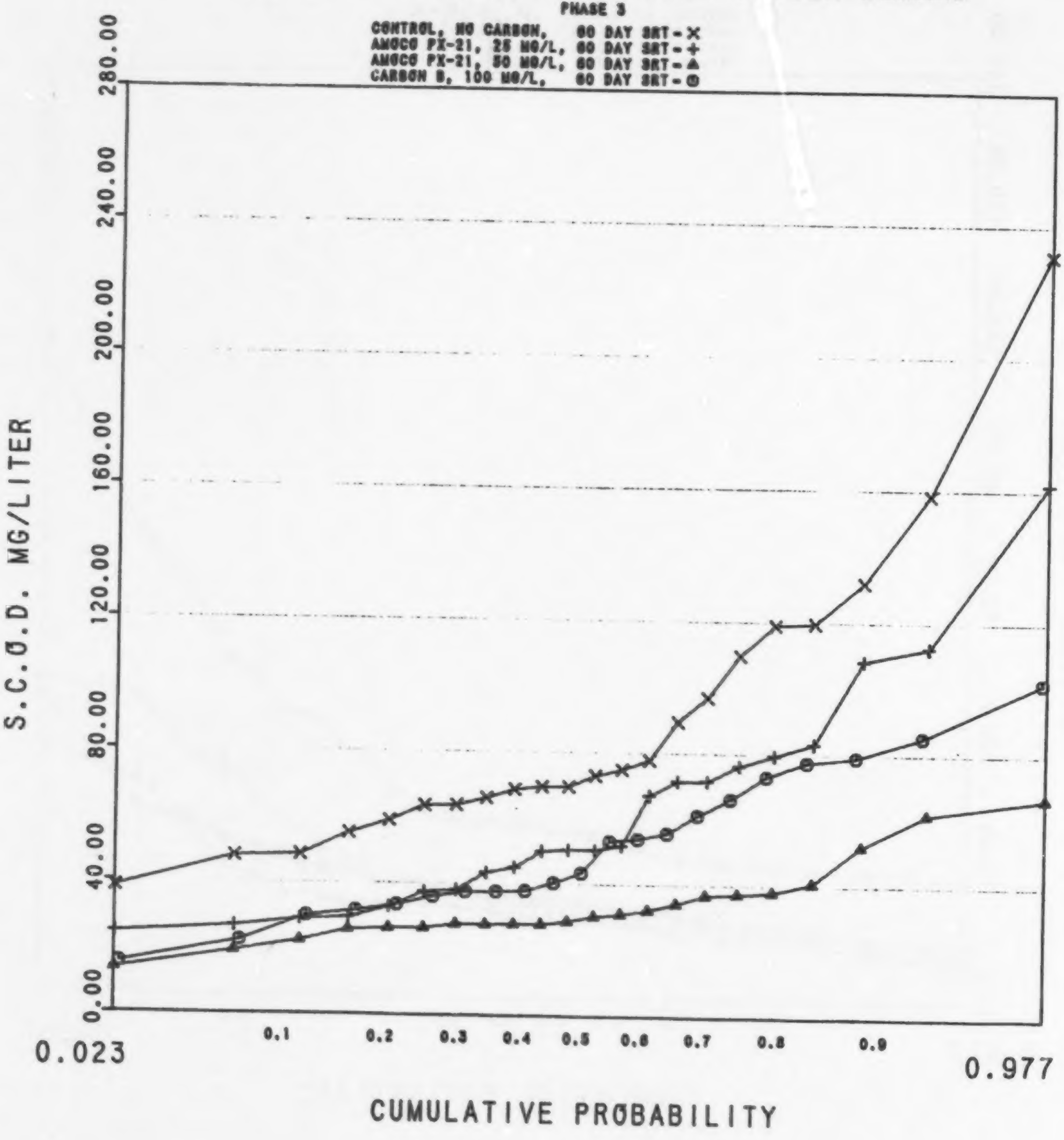


FIGURE 6 - AMMONIA-NITROGEN - PHASE 3

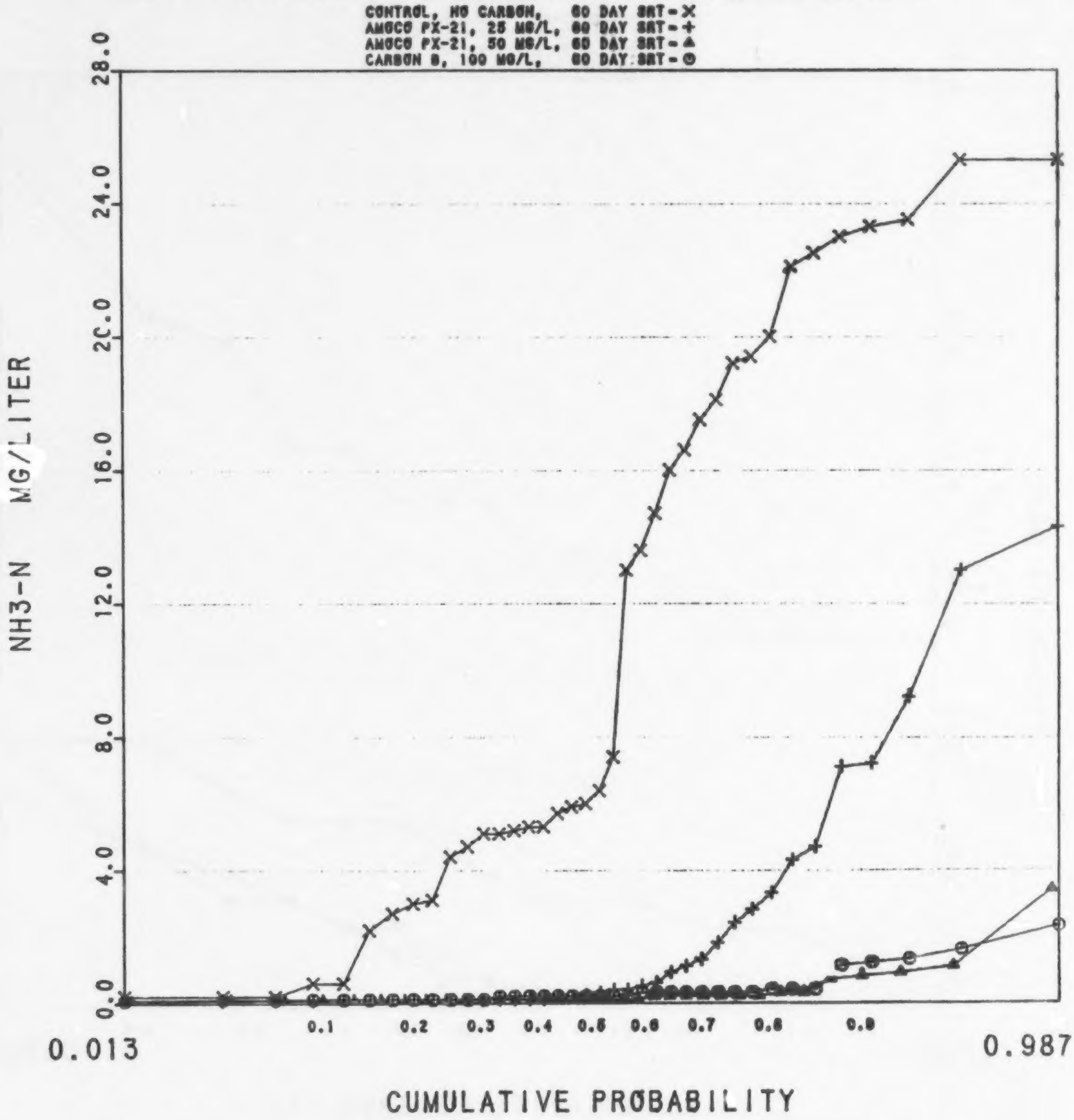
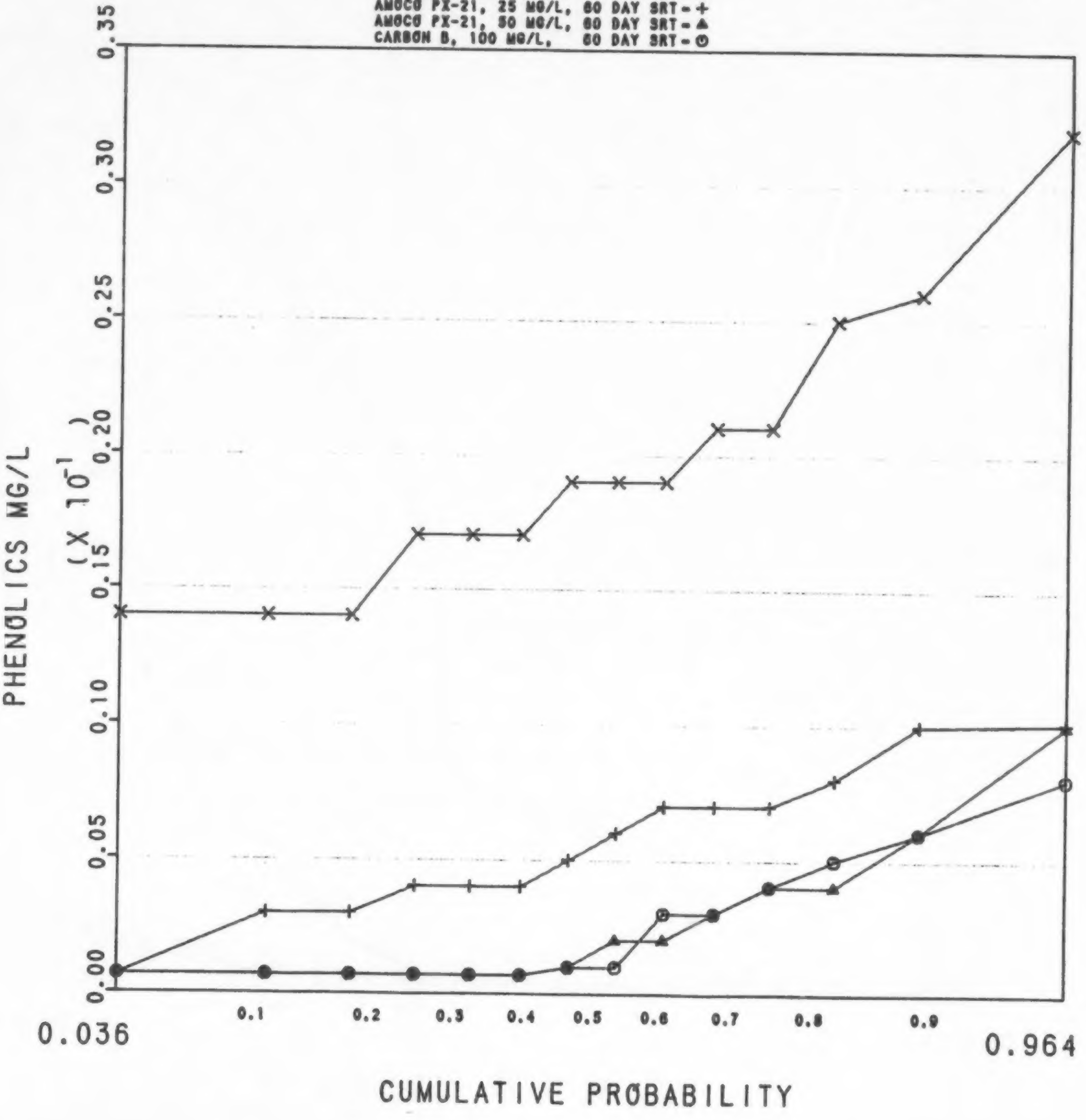


FIGURE 7 - PHENOLICS - PHASE 3



"TREATMENT OF OIL REFINERY WASTEWATERS WITH POWDERED ACTIVATED CARBON"

Paschal B. DeJohn
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INTRODUCTION

The effectiveness of powdered carbon as an additive to improve activated sludge treatment has been demonstrated in a variety of industrial and municipal plants. This type of treatment has gained wide acceptance in the past few years and is currently an essential part of treatment at 60-80 plants. These plants range in size from 10,000 gpd package units located along the Alaska Pipeline to the very sophisticated 40,000,000 gpd PACT treatment plant at the DuPont Chambers Works in Deepwater, New Jersey. At least four petroleum refiners currently use powdered carbon as an integral part of their waste treatment scheme.

HOW THE PROCESS WORKS

The reason powdered carbon has gained such acceptance treating a wide variety of waste streams is the extreme flexibility which can be employed in its usage.

- The amount of carbon used can be varied to meet the treatment requirements as they change.
- Higher COD or BOD removal than is usually obtainable by conventional biological treatment can be achieved.
- The combination of activated carbon in a biological system provides more effective treatment than either of the processes would if used singularly.

Carbon aids the biological process two ways:

1. By direct adsorption of pollutants.
2. By providing a more favorable environment for the microorganisms to propogate.

Adsorption is an equilibrium phenomenon. In general, carbon preferentially absorbs higher molecular weight compounds. Given a related series of organic compounds; for example, alcohols, one finds that the lower molecular weight alcohols (methanol, ethanol) are not appreciably absorbed by carbon while the higher molecular weight alcohols are. Fortunately, compounds which are poorly absorbed (weakly held by the carbon) are usually compounds which are the most amenable to biological treatment.

We can generally classify organic compounds into three broad categories with respect to their adsorptability onto carbon.

1. Compounds which are readily adsorbed. These compounds are usually "tightly held" by the carbon. And consequently, they are not readily desorbed.
2. Compounds which are adsorbed with difficulty. These compounds are desorbed easily.
3. Compounds which are poorly adsorbed.

Organic compounds can also be classified in terms of their susceptibility to biodegradation:

1. Compounds which are readily and rapidly biodegraded.
2. Compounds that are degraded slowly.
3. Compounds that are not biodegraded. Many of these can function as toxicants in a biological system.

It is important for one to understand the interaction of carbon and the microorganisms present in an activated sludge system. Exhibit 1 does this by considering how a carbon-biological system handles each of the above classifications of organics compounds. Relative adsorptivity and biodegradability for organic compounds was taken from an EPA source (Reference 1).

The boxes in Exhibit 1 have been numbered from 1 through 9 and are interpreted as follows:

Box	Degree of Biodegradability	Adsorptability
1	Rapid	Strong
2	Rapid	Moderate
3	Rapid	Weak
4	Slow	Strong
5	Slow	Moderate
6	Slow	Weak
7	None	Strong
8	None	Moderate
9	None	Weak

The classes of compounds which are represented by boxes 1, 2, and 3 would be handled quite easily by the microorganisms in a carbon-biological system. Those compounds which are represented by boxes 1, 4, and 7 would be removed by direct adsorption on the carbon. Compounds which fall in box 1 (both rapidly biodegradable and strongly adsorbed) are few in number. The only example that we could find is o-cresol.

Boxes 4, 5, and 6 represent compounds which are slowly biodegradable. These compounds probably would not be removed very effectively in a conventional activated sludge system. In a carbon-biological system, compounds in box 4 are removed by direct adsorption and are held very tightly by the carbon. Compounds in boxes 5 and 6 are retained in the system by moderate or weak adsorption. Because carbon is adsorbing these compounds, their concentration in the liquid stream is reduced. The microorganisms are able to degrade the organics in reduced concentrations, and as they do the equillibrium between the carbon and these organics in the waste is disturbed. Because these compounds are not held very tightly by the carbon, they are readily desorbed back into the system and a new equillibrium is established. In this fashion, the carbon is acting as a storage area keeping the concentration of slowly biodegradable organics at a level where they can be handled by the microorganisms. Compounds which fall into the categories represented by boxes 4, 5, and 6 are effectively handled in a carbon-biological system because of synergistic effects. It is primarily these compounds that are removed more effectively in a carbon-biological system as compared to either process operating singularly.

Compounds represented by boxes 7, 8, and 9 are not biodegradable. And in some cases, these compounds are actually toxic to microorganisms. In our opinion, carbon performs its most beneficial action in this area. Compounds which fall into the category represented by box 7 are removed by direct adsorption and are held very tightly by the carbon. Compounds in box 8 are removed by direct adsorption, and even though they are held very loosely by the carbon, it is difficult to disturb the equillibrium. This is because the concentration of these organics remaining in the waste stream are not being degraded by the microorganisms. The compounds represented by box 9 are the only ones that cannot be handled very effectively in a carbon-biological system. Fortunately, there are very few organics which are both non-biodegradable and weakly adsorbed by carbon.

Examples of the different compounds are shown in the various boxes in Exhibit 1.

One of the important effects of carbon in the system (not related directly to adsorption) is the higher levels of biomass that can be used because of the density and "weighting effect" of the carbon. (Both the use of greater sludge mass and the temporary retention of slowly degraded compounds by the carbon gives more time for the compounds to be consumed biologically).

Carbon adsorbs the pollutants and oxygen, localizing them for bacterial attack. Because the aerobic action is dependent upon the concentration of the reactants, this localizing effect serves to drive the reaction further towards completion resulting in improved BOD removal (Reference 2).

Many pollutants that are not biologically degraded in a conventional activated sludge system would be if they were in contact with the biomass for a longer period of time. When absorbed by the carbon, these molecules settle into the sludge. Contact time is thereby, extended from hours to days. This results in lower effluent COD's and TOC's. High density powdered carbons improve solids settling in the secondary clarifiers. This results in lower effluent suspended solids and also a reduction in BOD. Under high organic load conditions which normally would lead to sludge bulking, the dense carbon will act as a weighting agent keeping the sludge in the system. When dispersed biofloc results due to low organic loads, carbon serves as a seed for floc formation preventing loss of solids. Under these conditions, phosphorous and nitrogen removal are generally enhanced.

Powdered carbon improves treatment in activated sludge process because of its adsorptive and physical properties. Powdered carbon can be added to any convenient point in the activated sludge process to get it into the aerator. Direct addition to the aerator, sludge return lines, influent channels, or through the secondary clarifier are all possibilities. It is not necessary to add carbon continuously in most cases. A dense, easily wetted carbon can be added dry or in slurry form with water.

RESULTS

14 refineries have evaluated HYDRODARCO powdered activated carbons in full scale activated sludge systems during the past three years. The first treats a 2.2 MGD flow with an average BOD of 400 ppm in a 1.2 million gallon aerator. Mixed liquor solids are maintained at 3600 ppm (2880 ppm volatile). Waste activated sludge is digested aerobically, centrifuged, and hauled to landfill. Despite a secondary clarifier overflow rate of only 423 gallons/ft.^{2} and use of 22 ppm cationic polymer for secondary solids capture, effluent solids averaged in excess of 100 ppm. Toxic loads caused periodic loss of aerator biosolids. Defoamer costs averaged $200/day for aerator foam control.

HYDRODARCO C, a high density, lignite based powdered carbon, was added to the aerator over a four and one-half month period. Eventually, the equilibrium carbon level reached 1800-2000 ppm. At the sludge solids concentration obtained and wasting rates employed, it was possible to maintain this level with a daily average carbon dose of only 20 ppm.

Over the entire carbon test period, average BOD reduction equaled 82% versus 23% during the post test control period (Figure 1). As carbon built up in the system, BOD removals reached the 90-95% range, and the plant was able to meet their 30 ppm BOD effluent standard. Effluent COD was reduced from an average of 1180 ppm without carbon to 350 ppm with (Figure 2). Average effluent TOC decreased from 420 ppm to 100 ppm (Figure 3), and total carbon decreased from 520 ppm to 180 ppm (Figure 4). The lower slope of the carbon plots also indicate the decreased variability in effluent quality with carbon present.

HYDRODARCO C had a dramatic effect on the reduction of oil through the system (Figure 5). The effluent concentration was reduced by 75% (average), and the range was narrowed as well.

Both removal of the oil by the powdered carbon and the weighting effect of carbon resulted in lower effluent solids (Figure 6). Prior to carbon treatment, the plant used polymer at a dosage of 20 ppm, but still experienced poor solids settling. When carbon was added to the system, solids settling improved, and the polymer dosage was cut in half. Since effective solids settling could not be achieved with the use of carbon or polymer alone, it appears that the combination of the two was required to attain the desired results. This, of course, represents an operating cost savings for the plant.

Improved solids settling increased sludge thickening which allowed a 65% reduction in sludge wasting. Again, savings on the operation of the centrifuges, including power and labor, occurred.

Use of HYDRODARCO C eliminated the need for aerator defoamer. Removing the foaming agents from the wastewater by adsorbing them eliminated foam problems in the receiving stream. Defoamers only suppress foam in the aerator and do not prevent its reappearance in the effluent. Carbon can reduce operating costs by allowing surface aerators to aerate and mix the activated sludge rather than expand energy generating foam.

Both nitrogen (Figure 7) and phosphorous (Figure 8) removals were improved with powdered carbon. Reason: carbon adsorbs compounds toxic to nitrifiers and allows them to operate at normal levels. In this waste, neither nitrogen nor phosphorous were limiting for bacteria growth. Increased nitrogen removals are attributed to the fact that the dense carbon settled the nitrifying organisms which normally would float out of the system. The result is a longer solids retention time which is more favorable for nitrification to occur. By the same token, improved solids settling is probably the reason for decreased phosphorous levels. We suspect that the phosphorous is precipitated with the carbon-biosolids floc and removed in the sludge rather than degraded biologically.

While the exact reason for the bug kills prior to carbon was not known, upsets were greatly reduced with carbon in the aerator. A possible explanation is the effect carbon had on the removals of heavy metals such as zinc (Figure 9). The ability of activated carbon to adsorb heavy metals from wastewater has been established elsewhere (References 3, 4, and 5).

The second evaluation was conducted at a 12 MGD plant treating an average 12 MGD flow. The TOC of the raw waste ranged from 100-1000 ppm, averaging about 200 ppm. Major treatment problems included aerator foaming caused by alkanolamines in the waste; high effluent TOC; oily, difficult-to-handle sludge; and high effluent solids.

Effluent TOC's were maintained below 20 ppm during shock load periods. This was well within the standard of 50 ppm. In a post test control phase, a deterioration in effluent quality was observed as carbon was lost from the system through sludge wasting.

A third evaluation was conducted at a 2.5 MGD plant treating a 550 ppm COD refinery waste in a two stage, conventional activated sludge system. Carbon was added to the second stage aerator over a six week period. A constant daily carbon dose was maintained for each week and increased in succeeding weeks. No sludge was wasted intentionally during this time.

Optimum treatment was found at relatively high influent dose of 200 ppm. Effluent solids and COD removals increased 40%, and BOD removals, already high, increased 10%.

The major finding of this study was the increased removals of cyanide with carbon in the aerator. In conjunction with $CuSO_4$ treatment, the average cyanide levels decreased from 1 ppm before carbon to 0.05 ppm. The precise nature of this removal is not known and bears further investigation.

Results from a fourth study are summarized in Exhibit R for three separate carbon addition periods. This plant is a current user of activated carbon to treat 2.2 MGD flow. They have reported the following results from carbon addition (Reference 6):

56% reduction of suspended solids.
36% reduction of COD.
76% reduction of BOD.
Foam problem elimination.

This improved plant performance is achieved at a carbon cost of 1.7-4.3¢/1000 gallons treated.

A fifth study was made at a refinery which had a 6 MGD (8 MGD design) activated sludge plant. Carbon dosage reached approximately 500 ppm in the aerator before the study was terminated due to loss of biosolids. The loss of biomass resulted from an inadvertent increase in sludge wasting. This plant continued to use the same volumetric wasting rate when carbon was added to the system and because of the sludge density increase due to carbon addition, the MLVSS dropped sharply from 2900 ppm before carbon to 1500 ppm at the conclusion of the study. After carbon addition was stopped, the MLVSS returned to 2500 ppm with no change in the wasting rate.

Although considerable improvement in BOD removal was achieved at this plant (Exhibit S), the full benefit of carbon was not realized because of high influent oil concentrations (100+ ppm).

SUMMARY & CONCLUSIONS

- In summary, it has been shown that refinery wastes can be successfully treated with powdered carbon in activated sludge.

- Powdered carbon can improve organic removals, aid solids settling and sludge handling, and provide protection from toxic or shock loadings. In the face of widely varying influent organic or hydraulic loads, carbon levels effluent quality.

- High density carbons are preferred to minimize carryover from secondary clarifiers and to increase sludge compaction. Such carbons also require less makeup to maintain the desired aerator equillibrium level since carbon is lost from the system only during sludge wasting.

- Normally, one would think that the use of carbon would increase costs. However, savings on defoamers, coagulants, powder and labor can often decrease operating expenses.

BIOGRAPHY

Mr. Paschal DeJohn is Manager of Purification Sales and Project Leader in Activated Carbon at ICI United States Inc.; holding this position since 1972. Mr. DeJohn holds a B.S. degree in chemistry from Westchester State College and an M.B.A. degree from Widener College, Pennsylvania. Previous to his present position Mr. DeJohn was Water & Wastewater Treatment District Engineer with Drew Chemical, Parsippany, New Jersey. He is 1977 Technical Conference Chairman for WWEMI and the 1978 General Conference Chairman for this ame organization. Mr. DeJohn has been involved with water and wastewater treatment for the past twelve years.

James P. Black is Industry Coordinator for Water Purification at ICI United States Inc. He has a B.S. degree in chemical engineering from the University of Texas at Austin. Prior employment included ICI's Research & Development Laboratory, and Corporate Planning Staff.

DEJOHN PAPER DISCUSSION

Ed Sebesta, Brown & Root: Have you observed any situations where you mentioned some compounds are loosely adsorbed or difficultly adsorbed and then quite easy to be desorbed? Have you ever seen any situations or heard of situations where because of changing influent situations you may suddenly desorb an accumulation of adsorbed materials and effect the system in that way?

DeJohn: Potentially that can occur. I would think something like that would be more prone to happen in a granular carbon system. You can design a granular carbon system around this however. In the PACT systems we've been involved in, I'm not aware of any that have desorbed back an accumulation of adsorbed material. But there's always the possibility that this can happen.

REFERENCES

1. EPA Contract 68-01-2926, April 1, 1975.

2. Adams, A.D., "Improving Activated Sludge Treatment with Powdered Activated Carbon - Textiles" presented at the 6th Mid-Atlantic Industrial Waste Conference, University of Delaware, November 15, 1975.

3. Esmond, S. E. and Petrasek, A. C., "Removal of Heavy Metals by Wastewater Treatment Plants," presented at the WWEMA Industrial Water and Pollution Conference, Chicago, Illinois, March 14-16, 1973.

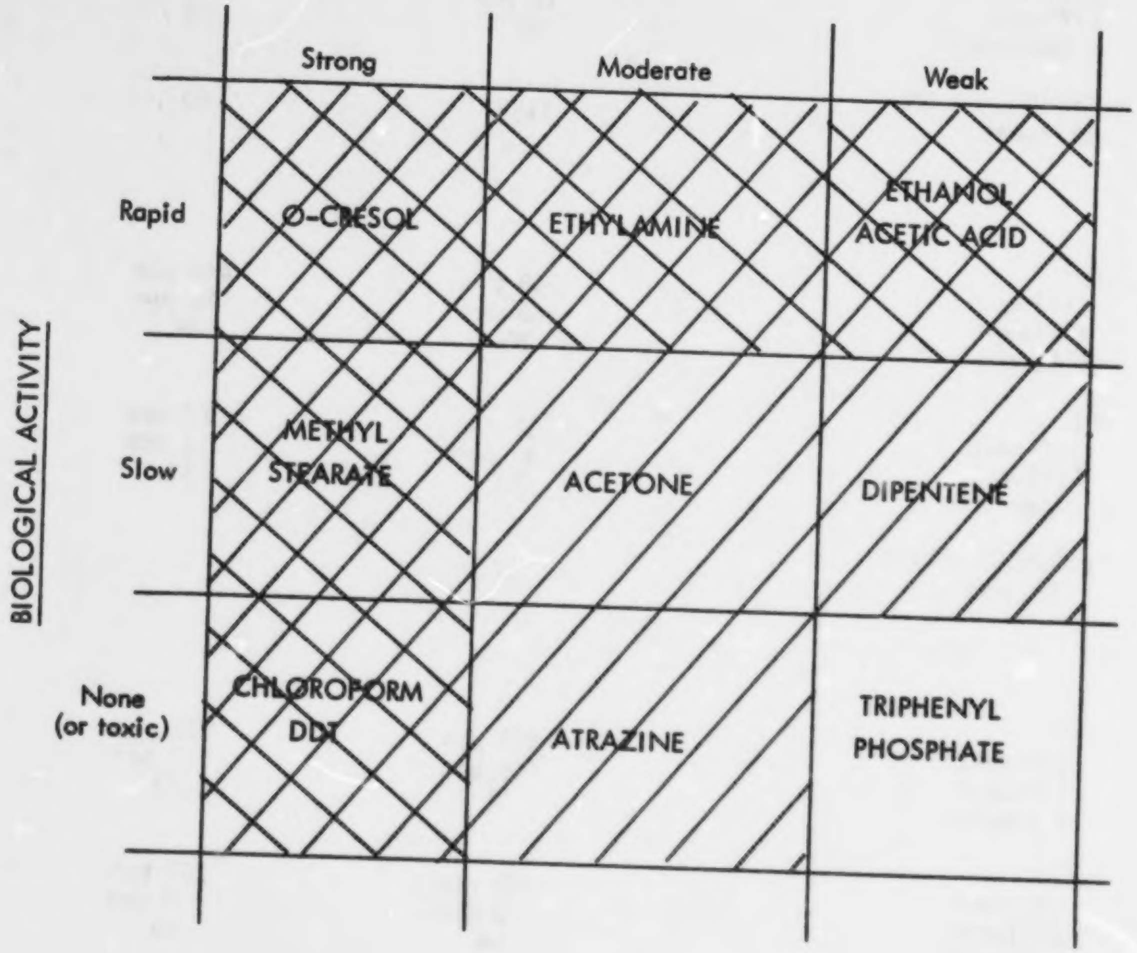
4. Sigworth, E. A. and Smith, S. B., "Adsorption of Inorganic Compounds by Activated Carbon," Journal AWWA, Water Technology/Quality, June, 1972 (p. 306).

5. Linstedt, K. D. et. al, "Trace Element Removals in Advanced Wastewater Treatment Processes," Journal WPCF, 43, No. 7, 1507 (July, 1971).

6. Rizzo, Joyce A., "Case History: Use of Powdered Activated Carbon in an Activated Sludge System", presented at the Open Forum on Management of Petroleum Refinery Wastewaters, Tulsa, Oklahoma, 1976.

EXHIBIT 1

CARBON ADSORPTION



BIOLOGICAL ACTIVITY	Strong	Moderate	Weak
Rapid	O-CRESOL	ETHYLAMINE	ETHANOL ACETIC ACID
Slow	METHYL STEARATE	ACETONE	DIPENTENE
None (or toxic)	CHLOROFORM DDT	ATRAZINE	TRIPHENYL PHOSPHATE

EXHIBIT R

	No Carbon	First Carbon Period
COD		
Influent	459 ppm	457 ppm
Effluent	170 ppm	135 ppm
% Removed	63	70
BOD		
Influent	152 ppm	213 ppm
Effluent	15 ppm	15 ppm
% Removed	90	93
SUSPENDED SOLIDS		
Effluent	115	50
COD		
Influent	343 ppm	444 ppm
Effluent	266 ppm	183 ppm
% Removed	23	59
BOD		
Influent	152 ppm	227 ppm
Effluent	30 ppm	14 ppm
% Removed	80	94
SUSPENDED SOLIDS		
Effluent	162	72
COD		
Influent	367 ppm	379 ppm
Effluent	166 ppm	112 ppm
% Removed	55	70
BOD		
Influent	188 ppm	207 ppm
Effluent	12 ppm	3 ppm
% Removed	94	99
SUSPENDED SOLIDS		
Effluent	79	42

EXHIBIT S

Flow: 8 MGD design, 6 MGD actual.

Carbon Dose: 500 ppm in aerator.

MLVSS: 2900 ppm before carbon
1500 ppm during carbon

(A 50% loss of aerator solids resulting from continuing same volumetric wasting rate of the more dense carbon sludge.)

2500 ppm after carbon

- BOD removal - 55% before carbon addition
  70-80% during carbon addition
  60% after carbon addition
- Influent oil concentrations were so high (100+ ppm) during test that effects of carbon were overshadowed.

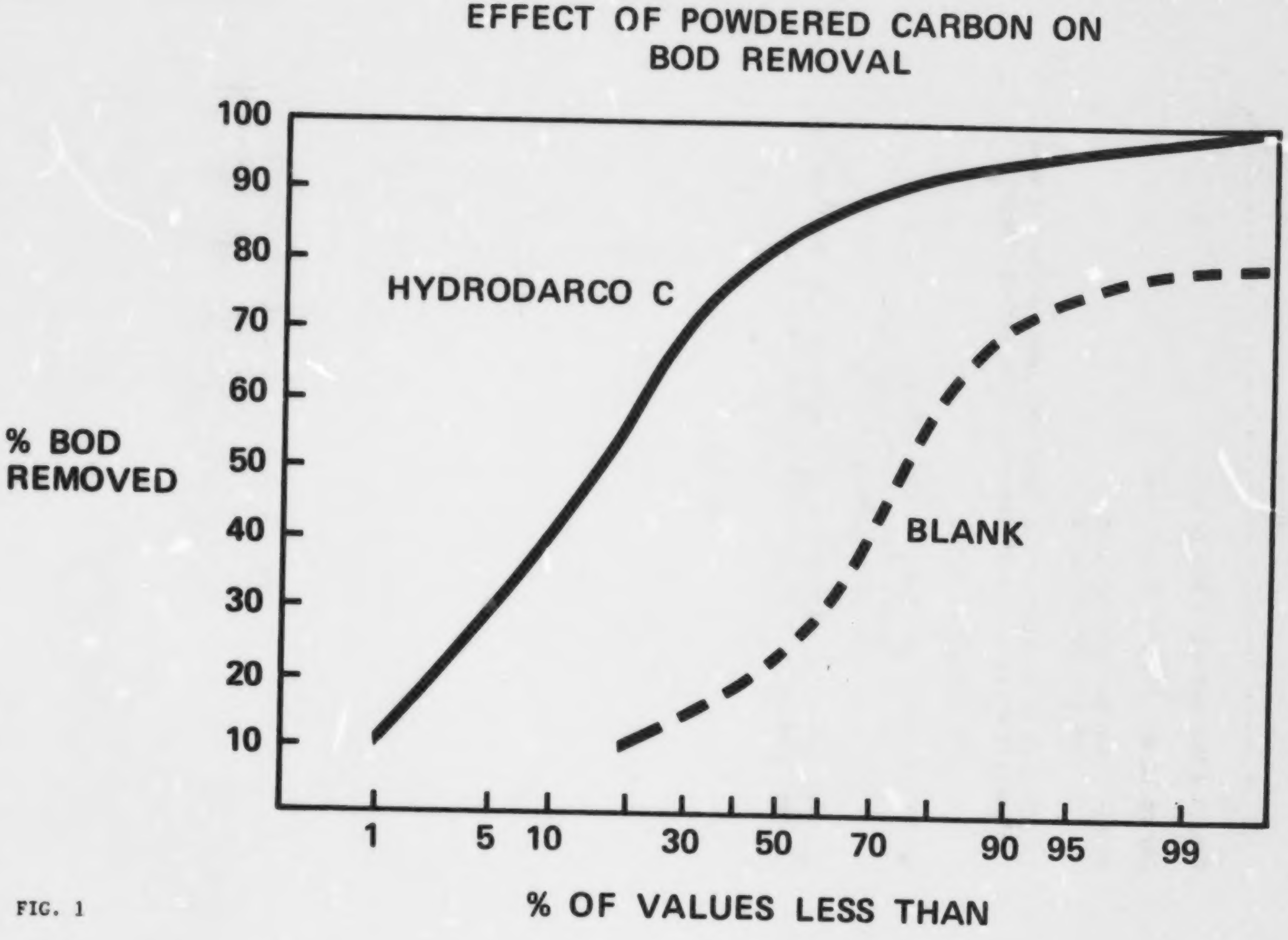
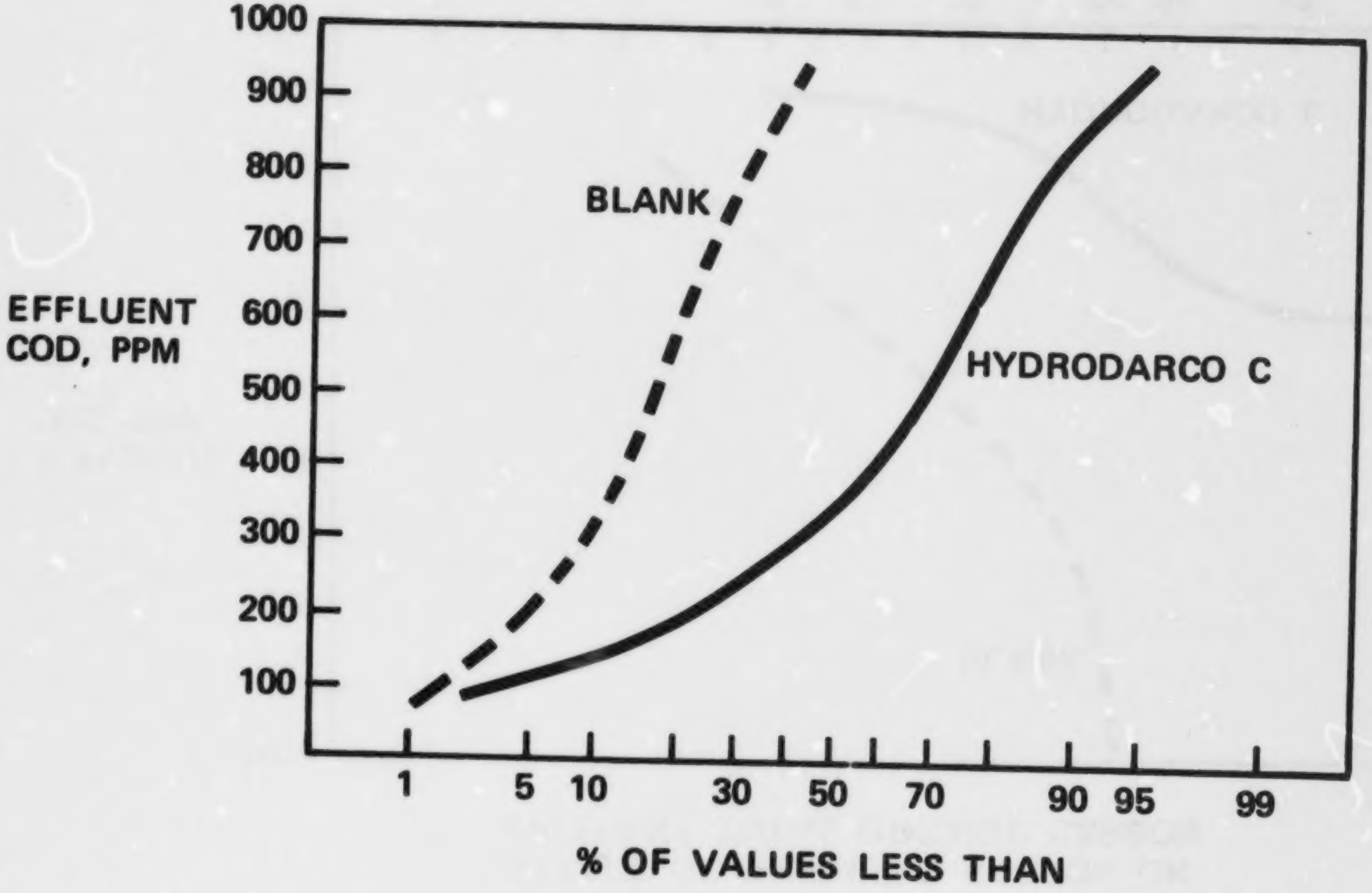

EFFECT OF POWDERED CARBON ON BOD REMOVAL
% BOD REMOVED
100
90
80
70
60
50
40
30
20
10
HYDRODARCO C
BLANK
1
5
10
30
50
70
90
95
99
% OF VALUES LESS THAN

FIG. 1

EFFECT OF POWDERED CARBON ON EFFLUENT COD



EFFECT OF POWDERED CARBON ON
EFFLUENT TOTAL ORGANIC CARBON

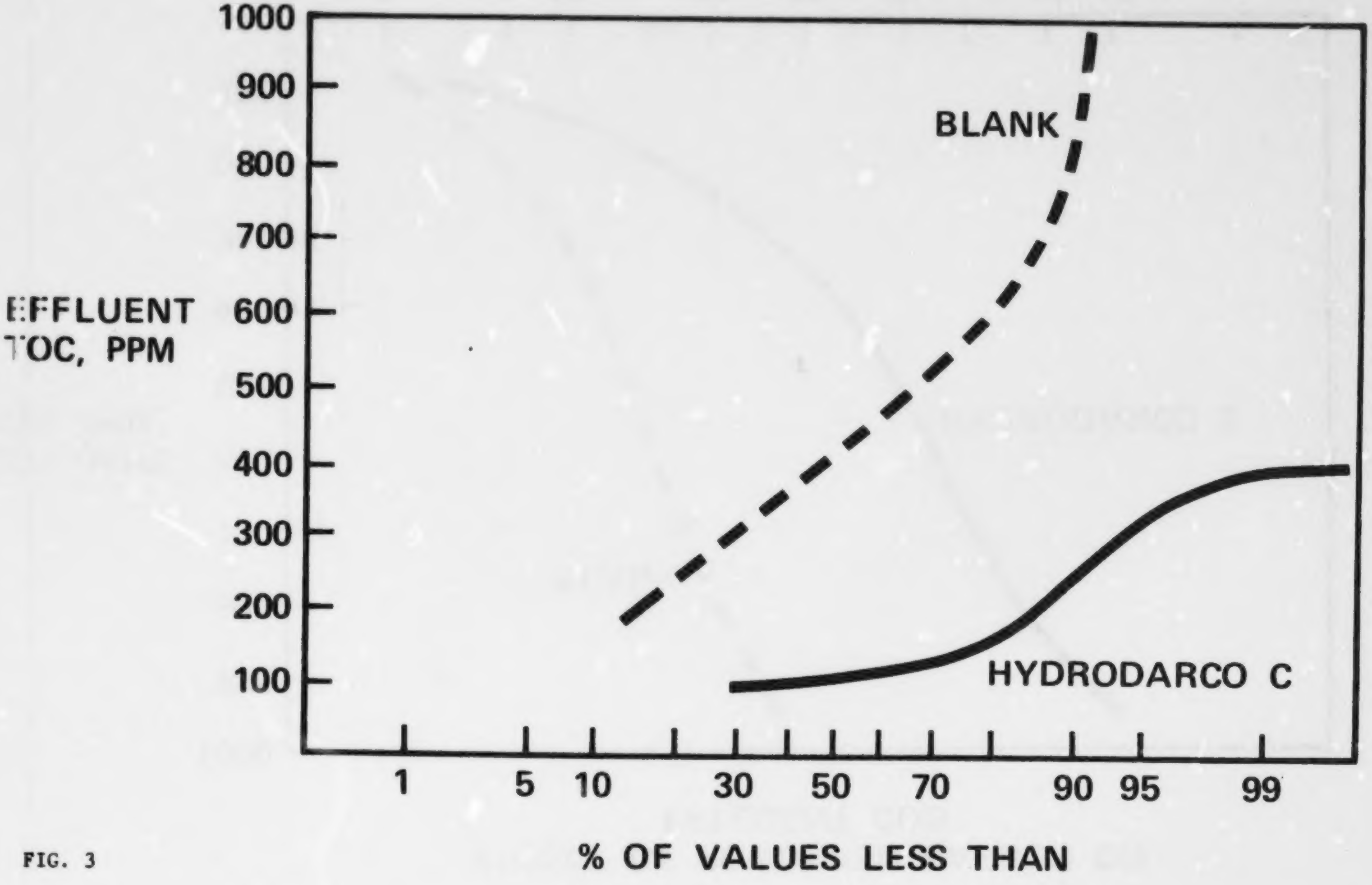
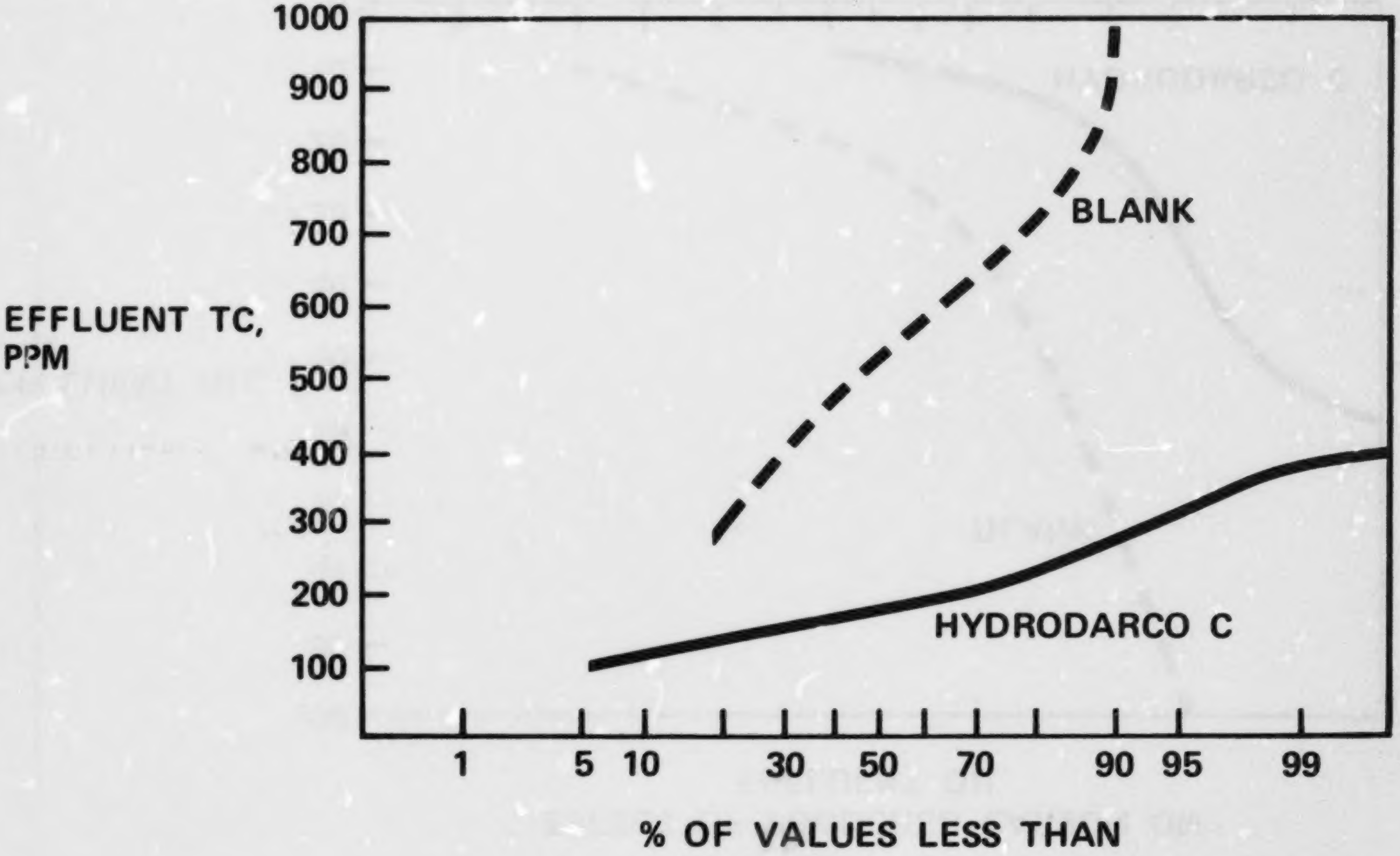
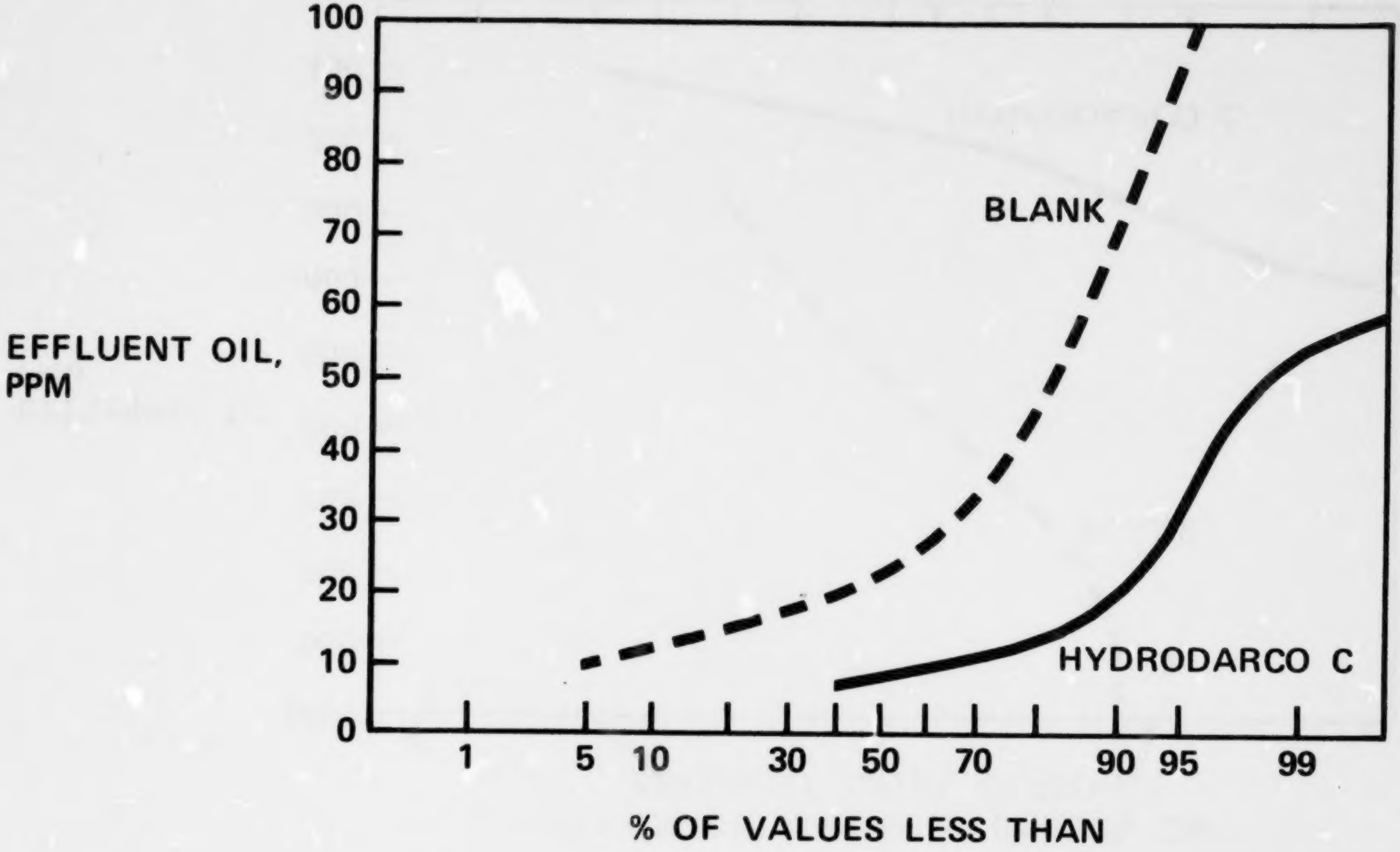


FIG. 3

EFFECT OF POWDERED CARBON ON EFFLUENT TOTAL CARBON



EFFECT OF POWDERED CARBON ON EFFLUENT OIL



EFFECT OF POWDERED CARBON ON
EFFLUENT SUSPENDED SOLIDS

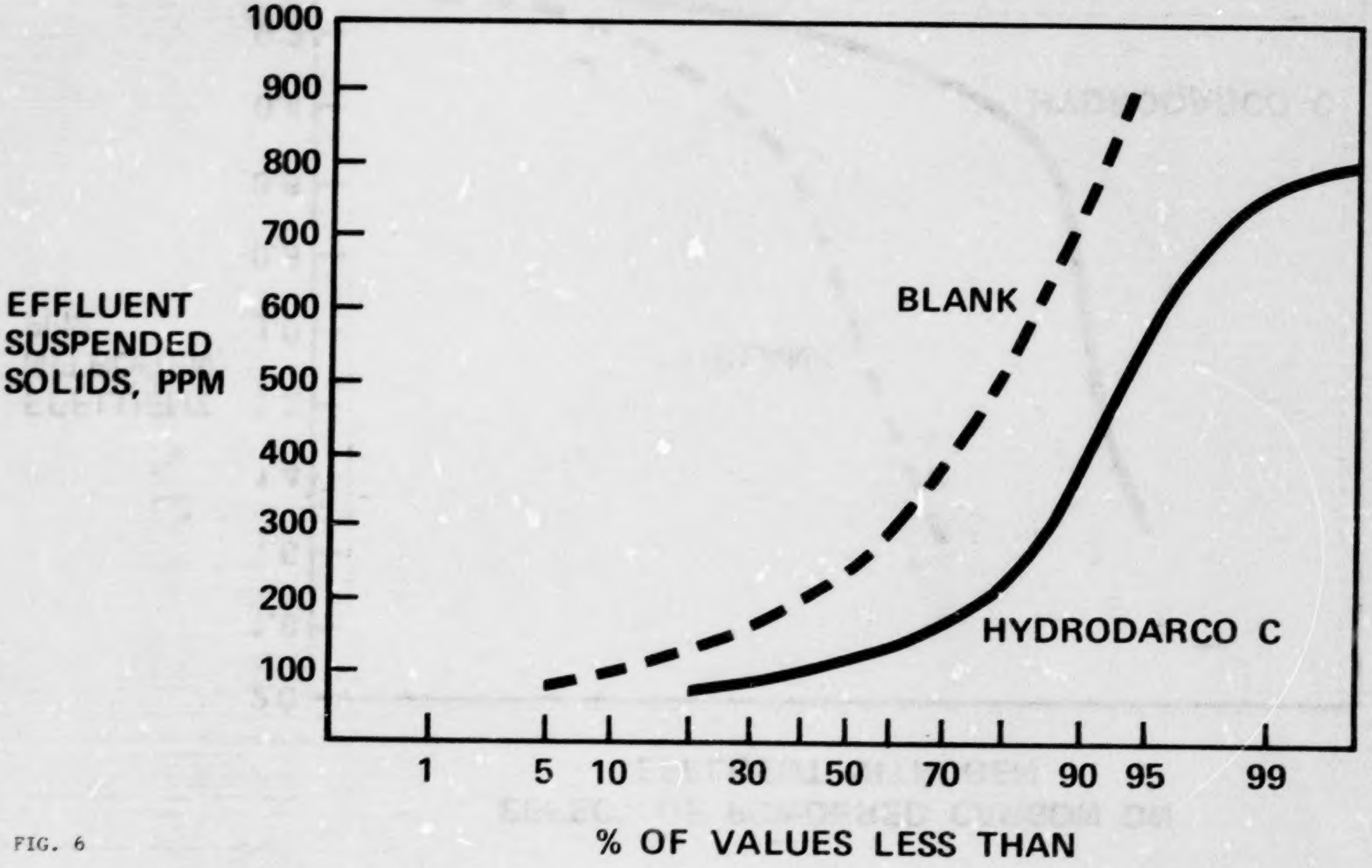


FIG. 6

EFFECT OF POWDERED CARBON ON EFFLUENT NITROGEN

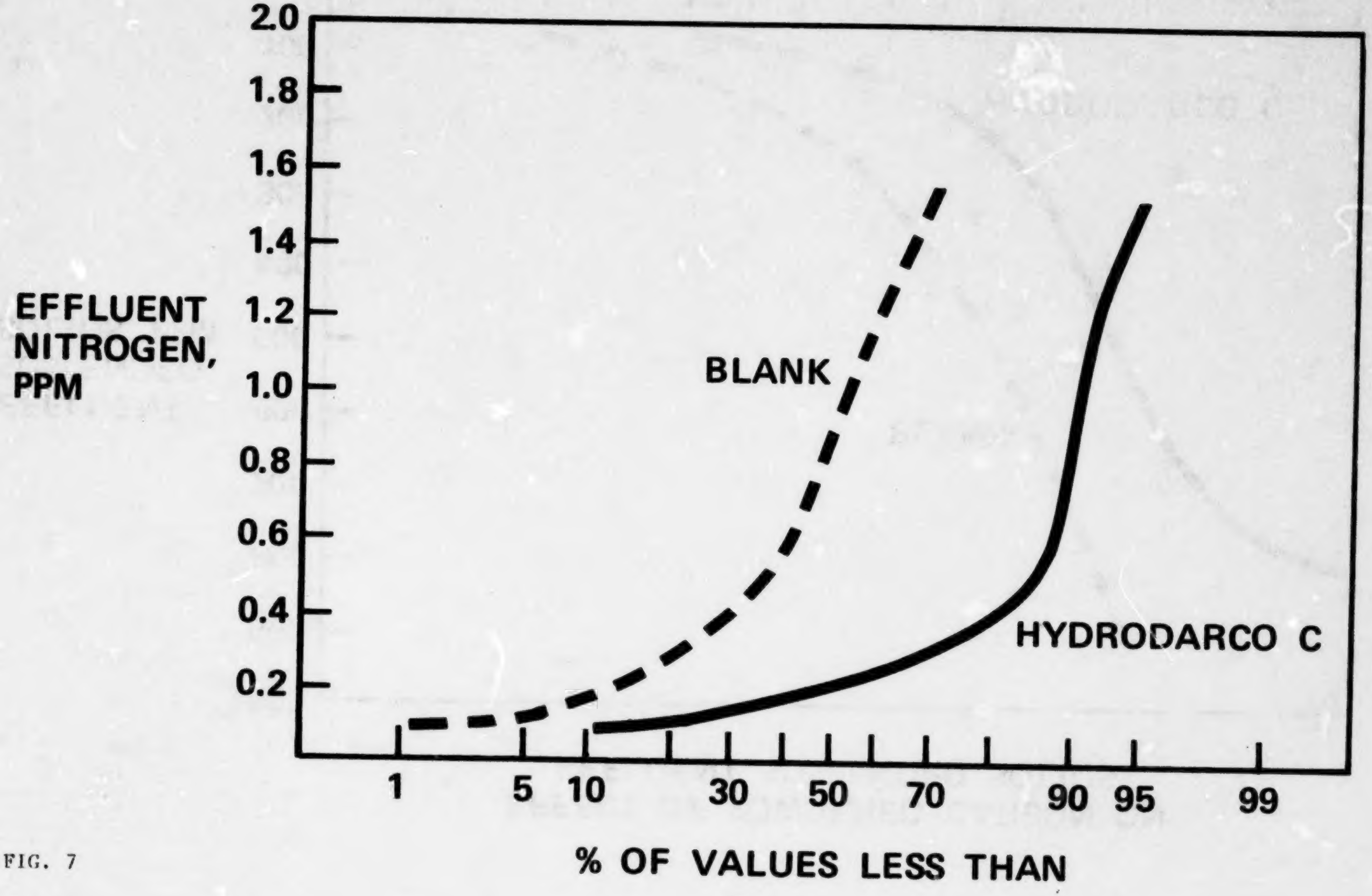
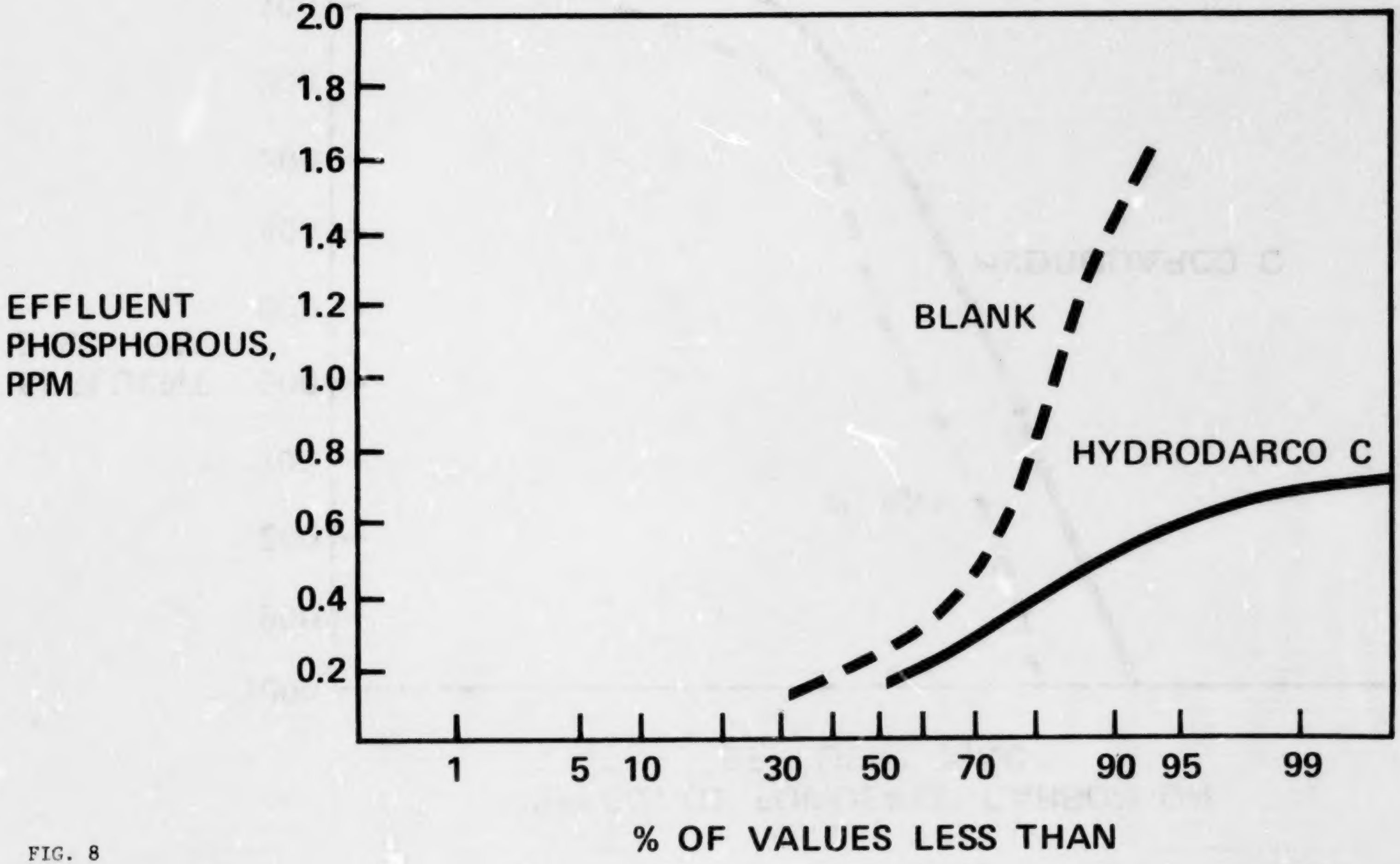


FIG. 7



EFFECT OF POWDERED CARBON ON EFFLUENT PHOSPHOROUS

FIG. 8

EFFECT OF POWDERED CARBON ON EFFLUENT ZINC

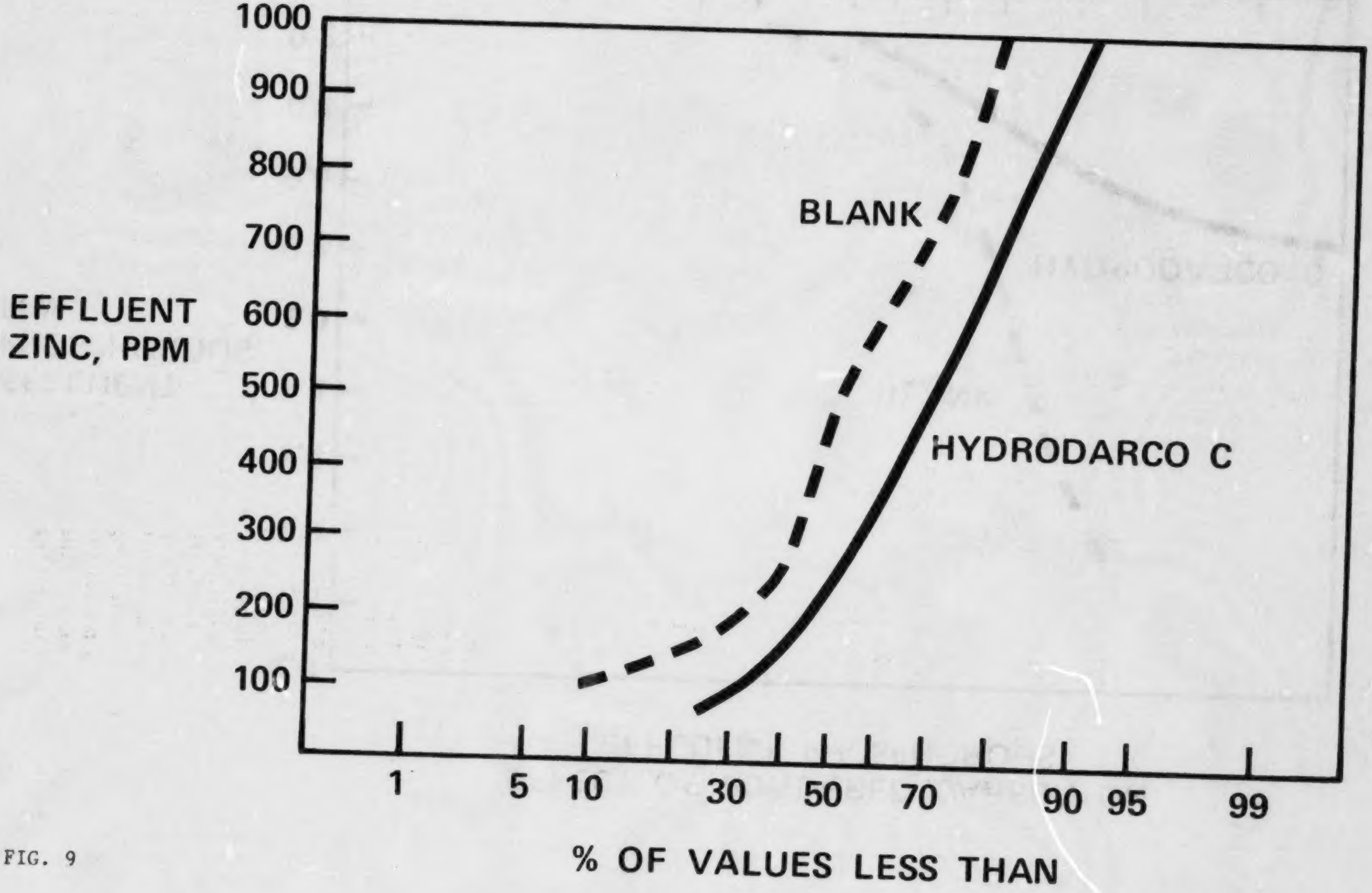


FIG. 9

CASE HISTORY
THE USE OF POWDERED ACTIVATED CARBON WITH A BIODISC-FILTRATION PROCESS FOR TREATMENT OF REFINERY WASTES

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ABSTRACT

A description of the development of a supplemental petroleum waste water treating plant utilizing a Rotating Biological Surface Unit and Powdered Activated Carbon followed by clarification and filtration from laboratory and pilot plant studies through construction, start up and operation to meet July 1977 NPDES discharge requirements.

Starting in 1972 Pilot Plant studies were conducted to compare the performance of activated sludge, trickling filter, RBS and activated carbon absorption processes in treating the Avon Refinery Waste Water. The primary objection was to meet the EPA guideline discharge limits plus the California State limits on fish toxicity. After several months of study the treatment scheme of a RBS Unit plus solids removal facilities was selected to meet the Federal standards and powdered activated carbon was selected to meet the toxicity limits.

INTRODUCTION

With the adoption of the 1972 Amendments to the Clean Water Act, the Staff at the Avon Refinery near San Francisco, then operated by Phillips Petroleum Co. embarked on an investigative program to determine the waste water treatment necessary to meet the limitations which would eventually be placed on the refinery discharge through the NPDES Program. At that time and until January 1975, the refinery discharge was already subject to limitations imposed by the California Regional Water Quality Control Board on 5-day BOD, oil and grease, settleable solids, suspended solids, coliform and fish toxicity. In addition, limitations were in effect on receiving water quality with respect to pH, dissolved oxygen, undissociated NH_4OH, chromium, lead, H_2S, Fish Toxicity, floating oil, discoloration or turbidity and odor. The existing waste water treatment included sour water stripping, API gravity separation, dissolved air flotation and pH equalizing surge ponds followed by a 108-acre bio-oxidation pond. The company had also segregated the refinery sewers so that as much as possible of uncontaminated storm run off could bypass the process water treatment. This storm run off was combined with the bio-oxidation pond effluent and discharged in an underwater diffuser in the main channel of an arm of San Francisco Bay which receives the Central California Valley drainage. This treating process is illustrated in Figure 1.

INVESTIGATION

At the start of the investigation, no specific Federal limitations had been determined and, therefore, the studies were mainly concerned with a comparison of generally accepted methods of waste water treatment to determine which of these would be most effective in removing or reducing the known pollutants in the Refinery effluent. A primary objective was to determine a treatment scheme that would result in a waste water discharge that would meet the more restrictive California State fish toxicity limitations that were being proposed.

In early 1972, working with an engineering contractor, three pilot plants were installed at the Refinery with a slip stream of the waste water going to the bio-oxidation pond serving as the raw feed. These units were an air agitated activated sludge unit, a 21-foot trickle filter and a four-column granular activated carbon unit preceded by a mixed media filter. These plants were operated from June 1972 through 1973 in parallel or in series under wide variations of operating conditions such as hydraulic loading, recycle rates and suspended solids concentrations.

During this period of operation, different sets of tentative EPA guidelines were issued for the Petroleum Industry. In each case, the effluent from the biological treating pilot plants failed to meet these guidelines and the proposed California fish toxicity standards. From the experimental data it appeared the only way these limitations could be met was by the use of activated carbon at high regeneration rates as a final treating step. It appeared that the waste water contained some non-biodegradable or at least "refractory" organic material as indicated by COD and TOC tests.

In the Spring of 1973, information was received describing the rotating biological surface units which were being proposed for treating industrial waste as an improved alternate to the other biological treatment systems. There were several advantages claimed for this process such as high biomass concentration; low volume, high density sludge production and low power requirement.

Subsequently, arrangements were made to install a four stage pilot rotating biological surface unit at the refinery and to compare its performance with the other pilot plants.

The RBS test program consisted basically of three periods determined partly by a difference in the quality of raw waste water and partly by the type of operation of the unit. During the first period, a direct comparison was made between the trickle filter, the activated sludge and the RBS units with the same feed going to all three units. For the second test period, the feed rate to the RBS unit was reduced to a very low figure to establish nitrifying bacteria in the bio-mass. During the third period, a series of hydraulic loading tests were performed where the rate was varied from 1/2 gpm to 18 gpm representing hydraulic loading of 0.2 to 6.8 gal/day/sq.ft. of surface area.

As a result of the pilot plant study, it was concluded that the removal of organic pollutants by the RBS unit compared favorably with the trickling filter and the activated sludge processes and, for some waste water parameters, the RBS unit appeared to be superior. The pilot plant operation verified most of the claims made by the manufacturer, particularly with respect to energy requirements and ease of operation.

The removal of organics by the RBS unit was very similar to the trickle filter and the activated sludge with each unit able to achieve about the same percentage removal and final concentrations in the final effluent at their optimum operation.

A portion of the test program was devoted to establishing nitrification and determining the relationship between hydraulic loading and the degree of conversion of ammonia to nitrate. This was accomplished by operating the unit at a very low feed rate and adding sodium bicarbonate to increase the alkalinity. At the low rate, it was possible to lower the ammonia concentration from 15 to 20 mg/l to less than 1 mg/l; however, as the feed rate was increased, nitrification decreased and eventually stopped altogether. Contrary to what was expected, over 50% of the conversion of ammonia to nitrate took place in the first stage. From the data obtained, it was concluded that, if nitrification is desired in a commerical unit, it would have to be designed for about one-half the hydraulic loading that would be required for organics removal.

One of the most noticeable differences between the RBS effluent and the effluent from the other bio systems was the suspended solids content. Although the suspended solids did increase with feed rate, even at relatively high hydraulic loading, the RBS effluent had lower suspended solids than the best operation of the other processes. At low feed rates, the RBS effluent after 30 minutes of settling, exhibited a sparkling appearance that was achieved on the other processes only by filtration or activated carbon treatment of the effluent.

Static bioassays were conducted weekly on samples of the various pilot plant effluents using the APHA standard methods to determine the 96-hr. median toxicity (TLm). Although the RBS unit was not the answer to the toxicity problem at the Avon Refinery, in general, this effluent was less toxic than the effluents from either the trickling filter or the activated sludge. Activated carbon absorption remained as the only waste water treatment that would produce a completely non-toxic water (100% survival) from the waste water stream.

Activated carbon treatment data are presented in Tables I through VIII.

Table I presents early data showing the effect on fish toxicity of treating various RBS effluents with powdered activated carbon.

Tables II and III present data on the effect of powdered carbon on other parameters and indicate that toxicity is improved although other parameters are not greatly affected.

Tables IV and V illustrate the effect of pH changes on toxicity and possibly the ability of carbon to absorb the toxicants.

Tables of VI and VII show comparisons of two different powdered activated carbons and indicate that selection of the proper carbon source can make a very great difference in the ultimate success of carbon treatment.

Table VIII is a part of a very large table of data obtained on a granular carbon test conducted over a six month period. It is presented to further illustrate that long after the carbon was "exhausted" with respect to COD removal it would continue to produce a non toxic effluent and that it could be rejuvenated by a hot water backwash.

By the time these pilot plant studies were complete, the final guidelines had been issued by EPA and the N.P.D.E.S. permit for the refinery had been issued by the Regional Water Quality Control Board. This permit outlined not only the discharge limits but a compliance schedule for submitting a conceptual plan, completion of Engineering, start of construction and completion of construction. At this time a thorough review was made of all the accumulated pilot plant data and the conceptual plan developed. It appeared that of the many parameters of water quality, COD, suspended solids and fish toxicity would control the design of the treatment system. Included in the consideration was the volume of water which varied considerably with the seasonal storm water entering the process or oily sewers, since practically all of the annual rainfall in this location occurs between the first of November and the first of April. Several alternate plans were considered but all were basically a supplemental biotreatment, solids removal and activated carbon treatment.

During the long period of monitoring the raw waste quality it became evident that treating requirements were also cyclic in that both COD and toxicity increased during the winter months but during part of the year the discharge would probably meet the 1977 limits without much, if any, additional treatment. In our studies with granular activated carbon we noted that in several instances long after the carbon was "exhausted" with respect to removal of COD it would still produce a non toxic water. From this information it appeared the biotreating system should be capable of handling wide variation in waste loading and that a carbon system should be designed to be used only when necessary. From Capital cost considerations, possible ease of handling and the indication that relatively small quantities would be required, the decision was made to use powdered carbon on a periodic and throw away basis rather than use a granular bed system.

In the summer of 1975 the conceptual plan illustrated in Exhibit II was put out for bids to Engineering-Construction Firms as a "turn key" project. As a result Engineering was completed by December 1975, field construction started in February 1976, and completed by January 1, 1977, all well within the compliance schedule.

At this writing the treating facilities are still in the process of starting up primarily because of an extraordinary length of time required for biomass to develop on the RBS units and then delays in correcting minor difficulties with certain mechanical equipment, instruments and electrical control systems.

Our principle concern was the difficulty in establishing the biomass. During the pilot plant phase we had started up three different pilot plants charging similar waste water and in all cases a good growth was established within 3 to 4 weeks. However, in the case of our commerical unit after four weeks there was only a very slight indication of biogrowth on the first stage. It was determined that low water temperature and relatively low soluble BOD were responsible for the apparent lack of bioactivity.

With increased temperature and the addition of higher strength waste water, supplied with a portable pump for 10 days, we observed an increase in the growth of the biomass extending through all three stages. Up to this point only the RBS and the clarifiers were in operation with the plant effluent returning to the feed surge ponds. However, with the establishment of biomass, the filter, polymer injection system and sludge digester were all put into operation. The carbon system was operated for a short period primarily to test it mechanically.

Only limited data has been obtained at this time however, they indicate the plant will perform satisfactorily and the waste water discharge will be in compliance with the July 1, 1977 limitation.

BIOGRAPHY James F. Dehnert

James F. Dehnert is the Environmental Director for the Avon Refinery of Lion Oil Company at Martinez, California. He has a B.S. degree in Chemical Engineering and a B.S. degree in Chemistry from Washington State University. He has been employed at this Refinery for thirty years with various assignments in Techanical Service, Economic Planning and Unit Operations. He served as an Area Operation Supervisor before becoming involved in Environmental assignments.

EXHIBIT I

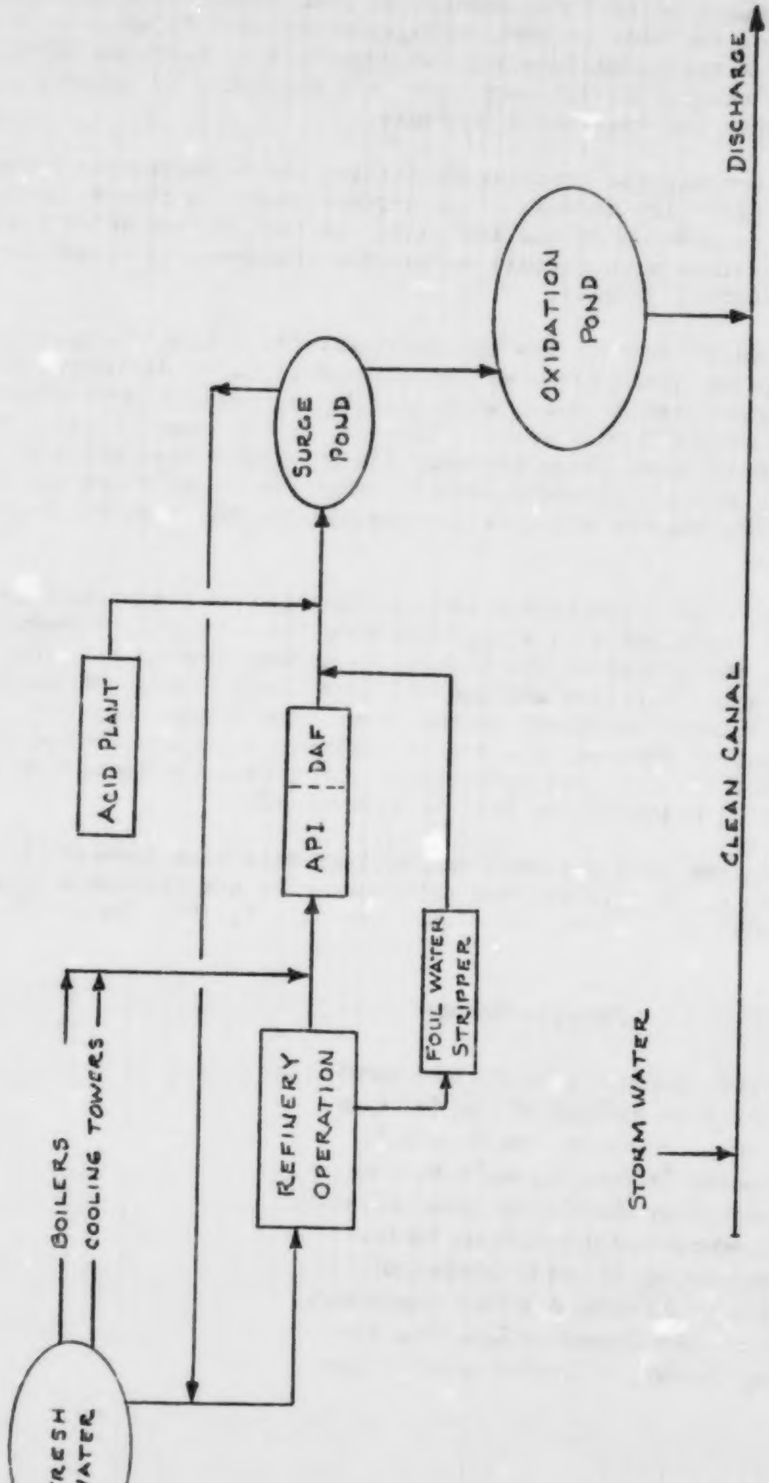
FRESH WATER
BOILERS
COOLING TOWERS
REFINERY OPERATION
FOUL WATER STRIPPER
API
DAF
ACID PLANT
SURGE POND
OXIDATION POND
STORM WATER
CLEAN CANAL
DISCHARGE

EXHIBIT II

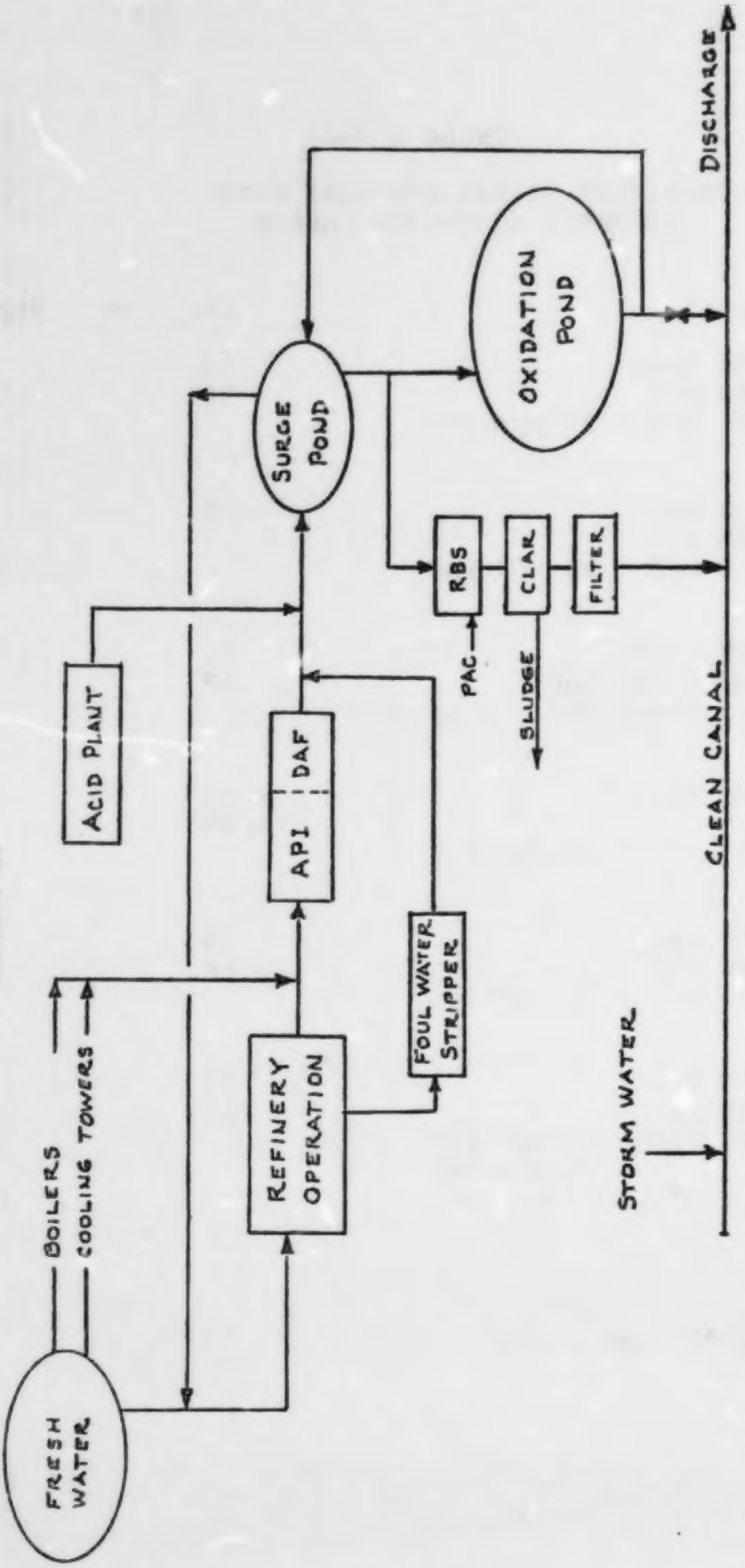
FRESH WATER
BOILERS
COOLING TOWERS
REFINERY OPERATION
FOUL WATER STRIPPER
API
DAF
ACID PLANT
SURGE POND
OXIDATION POND
RBS
CLAR
FILTER
PAC
SLUDGE
STORM WATER
CLEAN CANAL
DISCHARGE

TABLE 1

TREATMENT OF RBS EFFLUENT WITH POWDERED ACTIVATED CARBON

Test	Sample	TLm	or Survival*
No. 1	RBS Feed	74	
	RBS Eff	90	
	RBS Eff + 20 ppm PAC		90%
No. 2	RBS Feed	80	
	RBS Eff		90%
	RBS Eff + 10 ppm PAC		100%
No. 3	RBS Feed	80	
	2nd Stage RBS	92	
	2nd Stage RBS + 10 ppm PAC		90%
No. 4	RBS Feed	< 35	
	RBS Eff	< 75	
	RBS Eff + 10 ppm PAC		60%
No. 5	RBS Feed	33	
	RBS Eff	64	
	RBS Eff + 10 ppm PAC		60%
No. 6	RBS Feed	33	
	RBS Eff	>69	
	RBS Eff + 20 ppm PAC		90%
	" " + 35 ppm PAC		90%
	" " + 50 ppm PAC		100%

*Survival in undiluted waste

TABLE II

ACTIVATED SLUDGE EFFLUENT TREATED WITH PAC

Parameter		Act Sludge Eff	Act Sludge Eff +100 ppm PAC
Toxicity (% Survival)		0 (24 hr)	100 (96 hr)
COD	mg/l	108	84
NH_3(N)	mg/l	35	28
Oil	mg/l	0.2	0.1
Naphthenic Acids	mg/l	1.5	0.6
Cr(T)	mg/l	0.02	0.02
Cu	mg/l	0.20	0.25
Zn	mg/l	0.03	0.02

TABLE III

ACTIVATED SLUDGE EFFLUENT TREATED WITH PAC

Carbon Dosage (ppm)	0	50	100	150
Parameter				
Toxicity (% Survival)	0	10	100	100
COD mg/l	150	130	120	120
Phenol mg/l	4.8	4.9	4.7	5.2
Oil mg/l	0.1	0.1	0.1	0.1
Naphthenic Acid mg/l	3.1	4.3	3.5	3.1

TABLE IV

EFFECT OF pH ON TOXICITY

RBS Effluent @ 7.2 pH	40% Survival
RBS Eff Lowered to 6.5 pH	0% Survival
RBS Eff Raised to 8.5 pH	90% Survival

TABLE V

EFFECT OF pH ON CARBON TREATMENT

RBS Feed 7.1 pH	36 TLm
RBS Feed @ 6.5 pH + 30 ppm PAC	65 TLm
RBS Feed @ 7.0 pH + 30 ppm PAC	61 TLm
RBS Feed @ 7.5 pH + 30 ppm PAC	80 TLm

TABLE VI

COMPARISON OF TWO CARBONS

Sample	Toxicity	TOC (mg/l)
RBS Effluent (as is)	58 TLm	68
RBS Eff + 60 ppm PAC-A	85 TLm	57
+ 90 ppm PAC-A	93 TLm	57
RBS Eff + 15 ppm PAC-B	93 TLm	57
+ 30 ppm PAC-B	90% Survival	54
+ 60 ppm PAC-B	100% Survival	44

TABLE VII

COMPARISON OF TWO CARBONS

PAC-A Added Continuously to RBS Pilot Plant and Additional PAC-A or PAC-B Added to RBS Effluent

RBS Eff + 45 ppm PAC-A	40 TLm
RBS Eff + 195 ppm PAC-A	86 TLm
RBS Eff + 45 ppm PAC-A + 50 ppm PAC-B	93 TLm
RBS Eff + 45 ppm PAC-A + 75 ppm PAC-B	100% Survival

TABLE VIII

GRANULAR CARBON TREATMENT OF TRICKLING FILTER EFFLUENT

	COD mg/l					Toxicity (Survival)				
		Column					Column			
Day	Feed	No.1	No.2	No.3	No.4	Feed	No.1	No.2	No.3	No.4
1	180	70	60	30	10		100	-	-	-
2	180	80	30	30	30		100			
3	180	100	50	30	40		90			
4	200	120	50	30	50		70			
5	260	210	140	80	90		0			
6	300	260	160	110	100					
7	-	240	170	100	70					
8	-	250	200	140	100					
9	270	270	220	170	140			100		
10	320	300	250	210	170	61TLm		100		
20	220	210	170	160	100	34TLm		0	100	
30	180	130	130	120	110	71TLm			100	
45		160	160	130	130	45TLm			80	
50		170	170	150	130				0	0
	Hot Water Wash									
55	190	160	120	120	120					100
60	150	140	140	130	100	53TLm			100	100
70	150	150	140	140	140	59TLm			0	100
75	Hot Water Wash									
100	170	170	160	130	130	45TLm			80	100

SESSION VIII

ADD-ON GRANULAR ACTIVATED CARBON

Chairman

Nicholas D. Sylvester

Professor of Chemical Engineering
University of Tulsa, Tulsa, Oklahoma

Speakers

Fred M. Pfeffer

W. Harrison and L. Raphaelian

"Pilot-Scale Effect on Specific Organics Reduction and Common Wastewater Parameters"

R. H. Zanitsch

R. T. Lynch

"Granular Carbon Reactivation-State of the Art"

L. W. Crame
"Activated Sludge Enhancement: A Viable Alternative to Tertiary Carbon Adsorption?"

BIOGRAPHY Nicholas D. Sylvester

Nicholas D. Sylvester is Professor and Chairman of the Resources Engineering Division - Chemical and Petroleum Engineering - and Director of the Environmental Protection Projects program at the University of Tulsa. Dr. Sylvester received his B.S. degree from Ohio University, and his Ph.D. from Carnegie-Mellon University both in Chemical Engineering. Before coming to the University of Tulsa he taught at the University of Notre Dame. Nick is a member of the American Institute of Chemical Engineers, Society of Petroleum Engineers, American Chemical Society, Society of Rheology and the American Society of Engineering Education.

Professor Sylvester is currently conducting research in the following areas: two-phase flow, drag reduction, environmental protection, chemical reaction engineering and improved oil recovery. Dr. Sylvester has more than 50 technical publications and has been principal investigator of funded research totalling nearly $600,000.

In addition to his professional interests, Nick is active in youth athletic programs, having coached junior high basketball and elementary school baseball and soccer. He is also an avid, though inept, golfer.

ORGANICS REDUCTION THROUGH ADD-ON ACTIVATED CARBON AT PILOT SCALE

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Argonne National Laboratory
Argonne, Illinois 60439

ABSTRACT

The current wastewater BATEA model for the petroleum refining industry is the treatment sequence: activated sludge, mixed-media filtration, activated carbon. In an effort to develop data to assist in evaluating the model for specific organic compounds, the EPA (Ada, Oklahoma) entered into an Interagency Agreement with ERDA (Argonne National Laboratory) in January 1975. In cooperation with API, a .25 GPM pilot test was conducted at the SOHIO Refinery in Toledo, Ohio. Argonne followed with GC/MS analysis of samples collected across the treatment system to identify specific organics which are treatable versus those which pass-through (refractories).

The EPA's involvement included: the mobile pilot plant, refinery selection, conduct of the field study, sample preparation, and reporting. Argonne's analytical results showing a small overall reduction in organics by mixed-media filtration and a large reduction by carbon adsorption are discussed.

INTRODUCTION

In January 1975, the EPA (Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma) entered into an Interagency Agreement with ERDA (Argonne National Laboratory, Chicago) to develop data to assist in evaluating the performance of the BATEA model in the Development Document of 1974 (1). Since that time the BATEA regulations (and hence the BATEA model) have been remanded by a ruling of the 10th Circuit Court on the petition for revision of the guidelines by the API (2). However, the requirements for reconsideration and reissuing of guidelines as stipulated in the ruling, together with the mandates in PL-92-500 (Sec. 301. d.) (3), and the Settlement Agreement between EPA and NRDC (4), are added incentive to complete the work funded through this Interagency Agreement.

The proposed BATEA model was fixed bed carbon adsorption added onto the BPT model, which is biological treatment followed by granular media filtration. The specific treatment train selected for study was activated sludge, mixed-media filtration, and granular activated carbon. The performance criterion was to be the reduction of major organic compounds identified in the influent to the biological treatment system. Pursuant to the agreement, Argonne would perform qualitative organics analyses on samples provided by EPA. Pilot-scale filtration and carbon adsorption would be applied to the final effluent from a full-scale refinery treatment system. The results would serve as guidance for determining the need for larger-scale study and would not be used in predicting the performance of a full-scale add-on carbon system.

Refinery Selection

Considerable time was allocated to refinery selection as there was sufficient funding to study only one refinery. Repeated discussions and meetings were held with members of the API's W-20 Task Group to arrive at a "representative" refinery. It was agreed to acquire permission from a Class B refinery whose final effluent quality met BPT, with the possible exception of suspended solids. Other criteria would include intake water quality and variability, refinery turnaround plans, and final effluent quality, raw waste loading, and hydraulic detention times typifying the activated sludge process at a Class B refinery.

Agreement was reached in September 1976, to conduct the study at SOHIO's Toledo refinery. This is a Class B refinery (crude topping and catalytic cracking) with coking, having a crude capacity of 120,000 BPSD. The treatment train at that time consisted of the API Separator, dissolved air flotation (DAF), activated sludge (extended aeration) having 16-18 hours detention, and final clarification. The final effluent quality routinely satisfied BPT requirements with the exception of suspended solids. The refinery treatment system returned to steady state in November 1976, following a 1-month turnaround period.

The Pilot Study

A 30' EPA mobile trailer was transported to Toledo and positioned near the final clarifier. Facilities aboard the trailer included 6" I.D. glass columns for filtration and carbon adsorption (Figure 1), a TOC analyzer for monitoring organic carbon breakthrough, pumping and distribution capability, and sampling gear. The sampling equipment, pumps, and distribution lines were fabricated and installed such that the only materials in contact with water moving through the pilot treatment system were stainless steel, glass, Teflon, and polypropylene (Figure 1). Sampling points aboard the trailer were: 1) SOHIO's final clarifier effluent, 2) pilot mixed-media filter effluent, and 3) pilot carbon column effluent (Figure 2). The two remaining sample points were SOHIO's intake water and DAF effluent (Figures 3 & 4). These five points were sampled and iced on 4-hour intervals for 24-hour compositing over a consecutive 4-day period. During the study, there were no significant changes in recorded flows through the full-scale treatment system, as measured by the hourly biofeed pumping rates.

Two parallel down-flow mixed-media filters were utilized such that while one was operating for 24 hours, the second, having been backwashed, was ready for use the next day (Figure 5). Figure 2 shows the configuration of the filtering bed: anthrafilt, sand, and gravel. The sand used has an Effective Size = 0.2 mm and a Uniformity Coefficient = 4.5. Backwashing was accomplished by alternately pulsing with air and pumping carbon column effluent.

Two up-flow carbon columns (Figure 6) were packed as shown in Figure 2 and operated in series to achieve a total bed depth of 6 feet. A constant flow rate of 0.25 gpm was maintained, giving a residence time in the carbon bed of 36 minutes. The carbon used was Calgon's Adsorption Service Carbon. Calgon's analyses of a sample from the lot used at Toledo gave these results:

Apparent Density (gcc): 0.51
Molasses Number: 282
Iodine Number: 821
Sieve Result (mesh): 8x40

Attention was given to decontaminating material coming in contact with water samples. All glassware was cleaned by firing, maintaining 550°C for 1-hour. Sample bottle caps contained Teflon liners which had been cleaned by Soxlet extraction with methylene chloride--the solvent later used in the laboratory for extracting the organics from the water samples.

Each daily composited sample set was transported in ice chests to Detroit for air shipment. The samples arrived at RSKERL in Ada within 9 hours of final compositing in Toledo.

Laboratory Phase

Performance of the full-scale biosystem and the add-on filtration/carbon train for the common wastewater parameters is shown in Tables 1 & 2. Some values are reported as less-than (<), reflecting lower limits of detectability as a function of the sampling and analytical protocol.

Following the field study, the remaining responsibility of EPA was the preparation of the composited water samples for organics analysis by Argonne. This involved a tedious liquid-liquid extraction sequence using methylene chloride. Again, all glassware was fired for organics decontamination. A major problem was emulsion formation, requiring emulsion breaking and phase separation by various techniques. Each organic extract was dried by passing through anhydrous sodium sulfate and the solvent was stripped, resulting in 1-ml of concentrated extract which was sealed in a glass ampul. A period of 9 man-hours was involved in preparing each sample to the ampul stage; there were 20 samples requiring this preparation.

Gas-Chromatography/Mass-Spectrometry (GC/MS)

The samples supplied to Argonne for analysis consisted of 1 mililiter methylene chloride solutions of the acid, base, and neutral fractions composited over the 4-day sampling interval.

Analysis of the specific organics in these fractions was performed on a Hewlett-Packard Gas Chromatograph/Mass Spectrometer equipped with a data system and such peripheral equipment as a Zeta plotter and hard copy unit. Capillary columns were used in the gas chromatograph. These columns allow considerably greater separation and resolution of the organic components in a sample than do standard packed columns. Capillary columns also provide increased sensitivity and drastically reduced background from column bleed in the mass spectra. Also as opposed to typical GC/MS operation, no separator was used to remove the carrier gas. The outlet of the capillary column was connected directly to the source of the mass spectrometer and, therefore, there could be no discrimination in the amount of each component reaching the mass spectrometer. That is, assuming that the individual components in the mixture are not lost in the column, the effluent of the column and the amount of these components reaching the source of the mass spectrometer is a true representation of the quantities of compounds injected on the column. Finally, a Grob-type injection system was used in place of the inlet splitters typically used with capillary columns. The Grob system avoids the loss of large amounts of samples and the discrimination, typically found in split systems, of components of the mixture. It permits the analysis of minute concentrations of the specific organics present.

Figure 7 is a capillary column GC/MS total ion chromatogram of the neutral fraction of the dissolved-air-flotation effluent. It can be seen that there are over one hundred peaks or components in this fraction and that many of the components are present in minute quantities; that is, of the order of 200 ppt of the original water sample, assuming 100% extraction efficiencies. It was found that the organics in this neutral fraction of the DAF effluent were predominantly n-alkanes, alkyl benzenes, alkyl naphthalenes and polynuclear-aromatic hydrocarbons.

The activated sludge treatment system reduced the concentration of the organics in the DAF effluent by nearly 98%, as shown in Figure 8. It can be seen from the graphs that the peak height of several of the peaks in the FC effluent is approximately one-twentieth those in the DAF effluent, indicating there is approximately a twenty-fold reduction in pollutants by the activated sludge process.

Further reductions in organics were accomplished by the multi-media filter and the activated carbon column as shown in Figure 9. The concentration of the largest peaks of the compounds refractory to the add-on treatment system is of the order of 10 ppb. The percent reduction of the major classes of organics by the multi-media filter and the activated carbon column is as follows:

Compound	% Reduction
Alkanes	70-98
Alkyl Benzenes	35-90
Indenes	50-60
Indanes	76-96
Naphthalene	66
Alkyl Naphthalenes	65-90
Anthracene/Phenanthrene	86-93
Alkyl Anthracenes/Phenanthrenes	89-98
Other PNAs	96-98

It can be seen that there is generally greater than fifty percent reduction in these classes of organic compounds.

Work has not yet been completed on the acid and base fractions. Results will be available in a few months. The results of this study will be published as EPA and Argonne reports and as such will be available to the public.

It is expected that sufficient funds will be forthcoming in the next fiscal year to search and manipulate the data stored on disc for those consent-decree organics that may be present in these samples.

REFERENCES

(1) Development Document for Effluent Limitations, Guidelines and New Source Performance Standards for the Petroleum Refining Point Source Category, EPA-440/1-74-014-a, April 1974.

(2) Ruling of the 10th Circuit Court, Denver, on the suit of EPA by API, handed down August 11, 1976.

(3) Public Law 92-500, 92nd Congress, S.2770, October 18, 1972.

(4) Settlement Agreement in the U.S. District Court for the District of Columbia between the Natural Resources Defense Council and the U.S. EPA, Civil Action No. 2153-73, June 7, 1976.

ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance of the Calgon Corporation relating to activated carbon and the efforts of the API's Water Quality Committee and W-20 Task Group in arriving at a suitable refinery. We wish to thank Messrs. C. Tome, L.S. Van Loon, and J.H. Walters for assistance in the wastewater sampling program and Mrs. C.S. Chow for help with the GC/MS analyses. Most important, the study would not have been possible without the cooperation of SOHIO personnel at the refinery in Toledo and in the Department of Environmental Affairs in Cleveland.

DISCUSSION

Peter J. Foley, Mobil Oil: Would you comment on the contributions of the filter and the carbon columns in reducing organics?

Raphaelian: Although I do not have the exact numbers at hand, it appears to me that the multi-media filter had little or no effect on the concentration of organics whereas the activated carbon removed appreciable amounts of organics.

T. A. McConomy, Calgon Corp.: The naphthalene removal was only 66% as compared to more than 90% for other PNA's, why?

Raphaelian: These numbers are approximate figures based on the average of peak areas of individual components. Generally, one can say that those organics that have a long alkyl chain such as an alkane or an alkylated PNA are adsorbed on the carbon whereas parent PNA's are not. This is, of course, a crude approximation. We are still trying to get better gas chromatograms because all of these results are dependent upon how well you separate the compounds.

N. F. Seppi, Marathon Oil: Please comment on methylene chloride purification - also what about decomposition products from methylene chloride under basic conditions?

Pfeffer: Regarding the purity of methylene chloride, we relied upon the glass distillation procedures of the manufacturer (Burdick and Jackson). In addition, Argonne received a blank extract obtained by taking a high purity water and performing the acids, neutrals and basic extractions. This blank would also account for laboratory contaminations. I cannot offer any information about alkaline decomposition products.

Anonymous: Is there additional data from industry on the study at Toledo?

Pfeffer: I do not know. Both Exxon and SOHIO conducted parallel work to our own, presumably into the realm of GC mass-spec. We would entertain comparing notes with Exxon and SOHIO at some later date in order to validate what actually took place in Toledo.

Judith Thatcher, API: I noticed that the TOC of the influent water is very close to the TOC of the final effluent. Have you done any identification in the organics in the influent water to the refinery?

Pfeffer: We are looking at it, but haven't identified all the components yet.

Arthur J. Raymond, Sun Oil Co.: What phase was used on the capillary columns, and did you notice that your highly branched-chains were degraded much faster than the less branched? Also, was benzene degraded much faster than toluene and xylene?

Raphaelian: I don't understand what you mean by degraded.

Raymond: Did they decompose faster or disappear or reduce? Not in the column but in your system as you went from the influent water to the final clarifier. If you had percent reductions, which compounds went faster than others?

Raphaelian: I am still putting all this data together. However, I can say that it appears that the branched-chained alkanes, which were present in smaller quantities than the straight-chained alkanes, were not removed as well by the treatment system as the straight-chained alkanes. Because of the minute quantities of pollutants present, I am presently doing single-ion monitoring to try to get a better idea of the percent reduction across the treatment system.

Raymond: What phase did you use on a capillary column? What coating?

Raphaelian: For the work presented in this talk, OV-101 was the liquid phase and the columns were wall coated open tubular (WCOT) and not support coated open tubular (SCOT) capillary columns. It is difficult with OV-101 to get symmetrical peaks with polar compounds, that is, peaks without tailing. I used FFAP capillary columns for the acid and base fractions. By the way, we see a variety of alkylated phenols in the acid fraction.

Ed Sebesta, Brown & Root: I noticed that for TSS there is no decrease across the filter. Do you have any explanation for that?

Pfeffer: My only explanation is that considering the flow rate and sand specifications, the TSS coming from the final clarifier were such that the filter was ineffective. Also, at the 10 mg/l level, differences are probably within the experimental error of the test procedure.

BIOGRAPHIES

Fred M. Pfeffer holds the BA and MS degrees in Chemistry from the University of Cincinnati. He is currently a Research Chemist at the EPA's Robert S. Kerr Environmental Research Laboratory at Ada, Oklahoma.

Wyman Harrison holds the SB, SM, and a PhD degree in Geophysics from the University of Chicago. He is currently the Assistant Director of Applied Geoscience and Engineering, Energy and Environmental Systems Division at the Argonne National Laboratory, Argonne, Illinois.

Leo Raphaelian holds the AB degree from Harvard University and the MA and a PhD degree in Chemistry from Yale University. He is currently Manager of Environmental Sciences, Energy and Environmental Systems Division at the Argonne National Laboratory, Argonne, Illinois.

Table 1. DAILY PERFORMANCE FOR COMMON WASTEWATER PARAMETERS

	MG/L INTAKE				MG/L DAF EFFLUENT				MG/L FC EFFLUENT			
	Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4
Oil & Grease	<10	<10	<10	<10	22	33	21	22	<10	<10	<10	<10
Cyanide	<0.02	<0.02	<0.02	<0.02	0.19	0.25	0.31	---	0.16	0.12	0.20	0.10
Phenol	0.03	<0.01	0.03	0.01	320	260	520	450	0.02	0.01	0.04	0.02
COD	<15	18	<15	<15	122	172	154	154	49	50	51	44
BOD	<10	<10	14	<10	82	127	108	96	<10	15	21	24
TOC	19	19	17	15	39	56	72	60	22	29	27	17
TSS	35	29	11	<10	31	56	37	30	12	<10	<10	<10

	MG/L FILTER EFFLUENT				MG/L CARBON EFFLUENT			
	Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4
Oil & Grease	<10	<10	<10	<10	<10	<10	<10	<10
Cyanide	0.16	0.15	0.20	0.10	<0.02	<0.02	<0.02	<0.02
Phenol	0.02	0.01	0.02	0.02	<0.01	<0.01	<0.01	<0.01
COD	42	38	51	44	<15	<15	<15	<15
BOD	<10	11	22	27	<10	<10	<10	<10
TOC	19	26	23	18	10	12	11	<5
TSS	<10	<10	12	12	<10	<10	<10	<10

Table 2. AVERAGE PERFORMANCE OVER 4-DAY STUDY PERIOD FOR COMMON WASTEWATER PARAMETERS

	MG/L INTAKE	MG/L DAF	MG/L FC	MG/L FILTER	MG/L CARBON
Oil & Grease	<10	24	<10	<10	<10
Cyanide	<0.02	0.25	0.14	0.15	<0.02
Phenol	0.02	390	0.02	0.02	<0.01
COD	<15	150	48	44	<15
BOD	<10	103	17	17	<10
TOC	18	57	24	22	9
TSS	21	38	<10	<10	<10

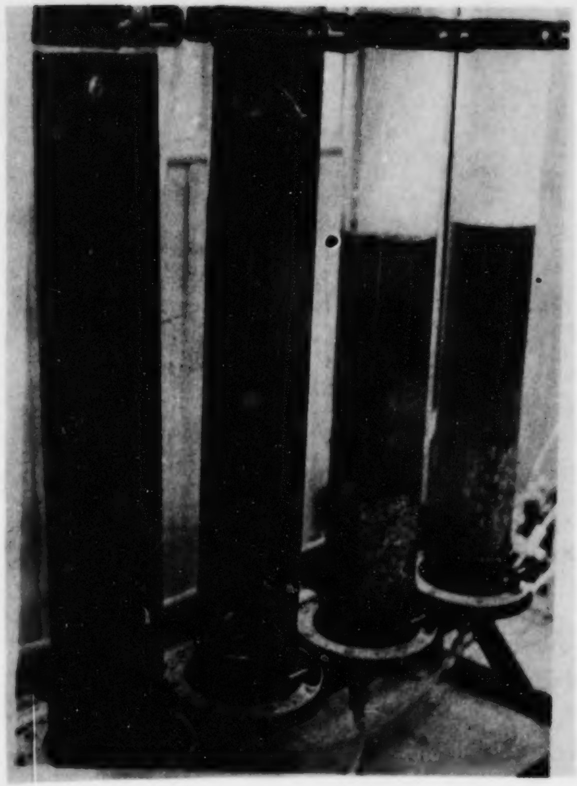


Figure 1. CARBON COLUMNS

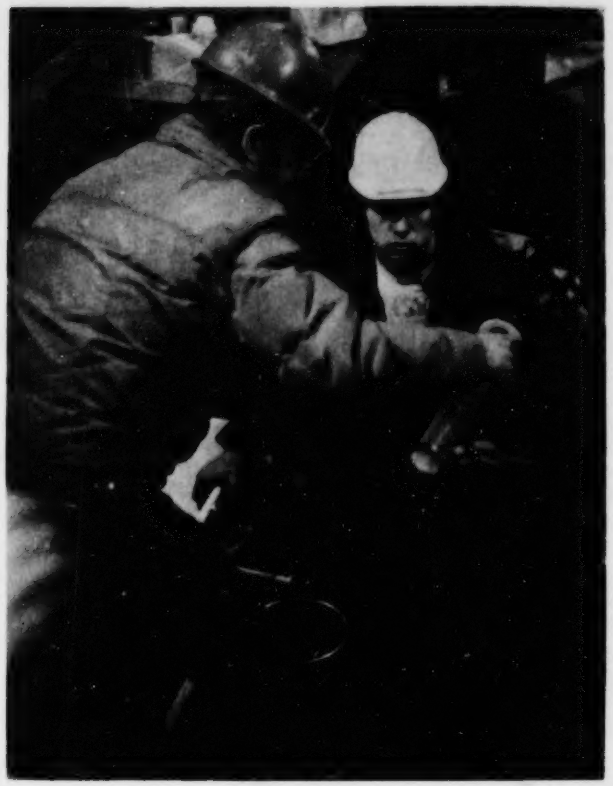


Figure 3. SAMPLING POINT: PLANT INTAKE

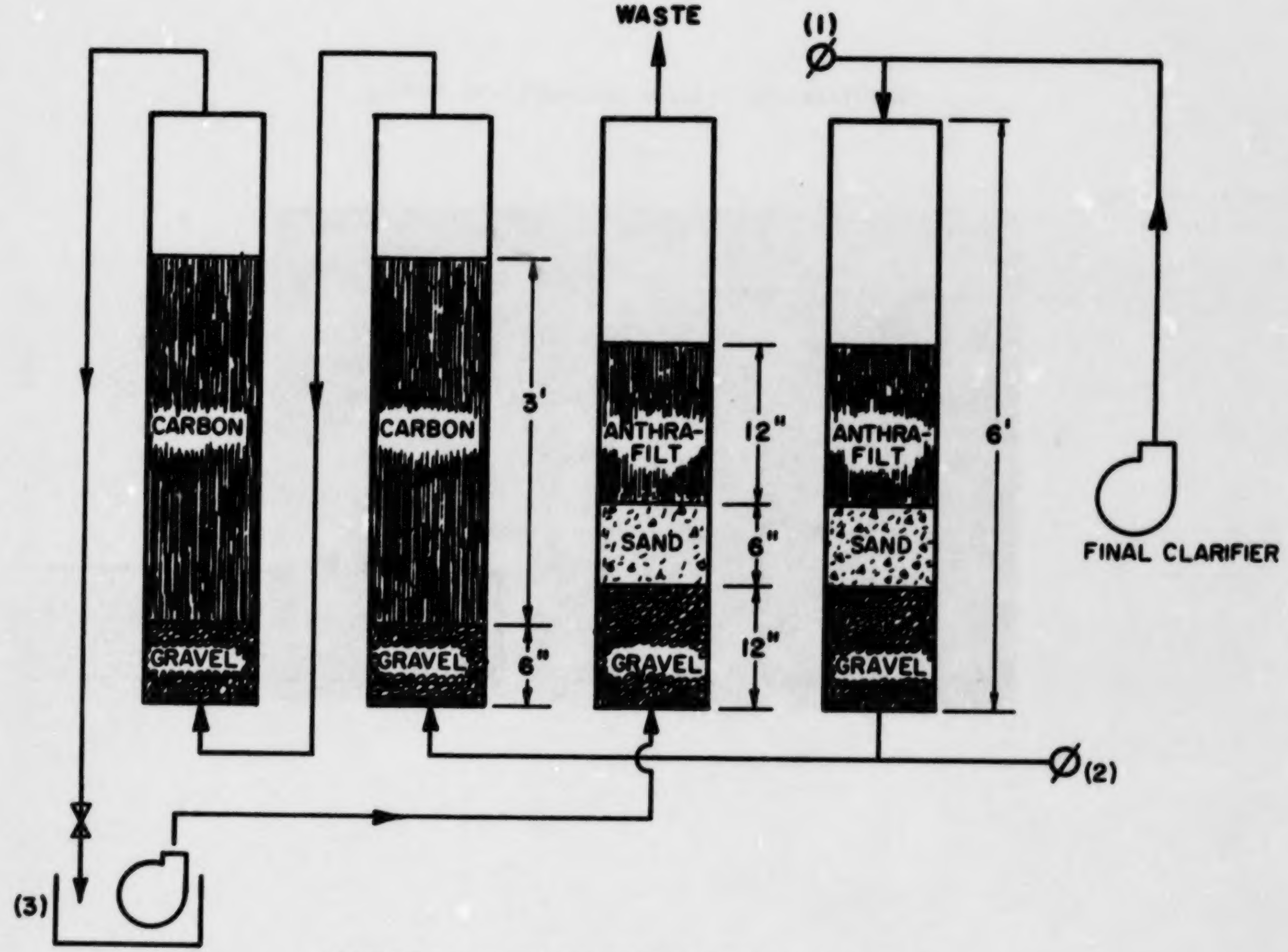


FIGURE 2 - PILOT TREATMENT FACILITY

Figure 4. SAMPLING POINT: DAF EFFLUENT

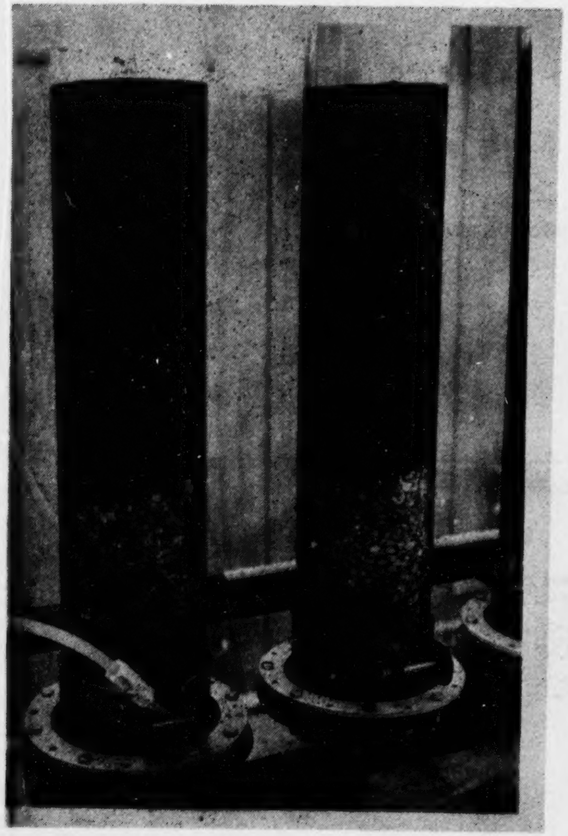


Figure 5. MIXED MEDIA FILTERS

Figure 6. CARBON COLUMNS

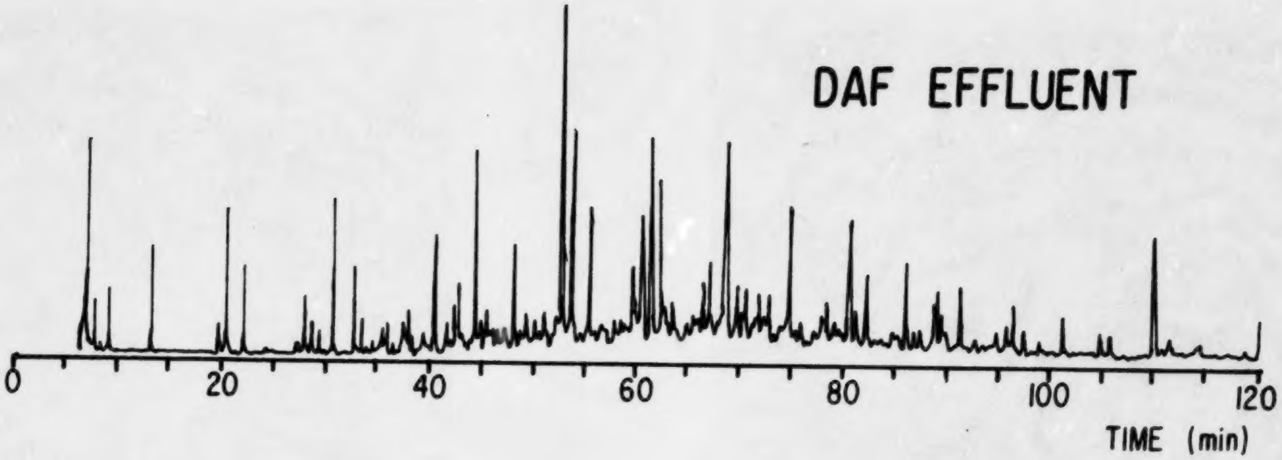


Figure 7. Total Ion Chromatogram of DAF Effluent (Neutral Fraction, Four-Day Composite)

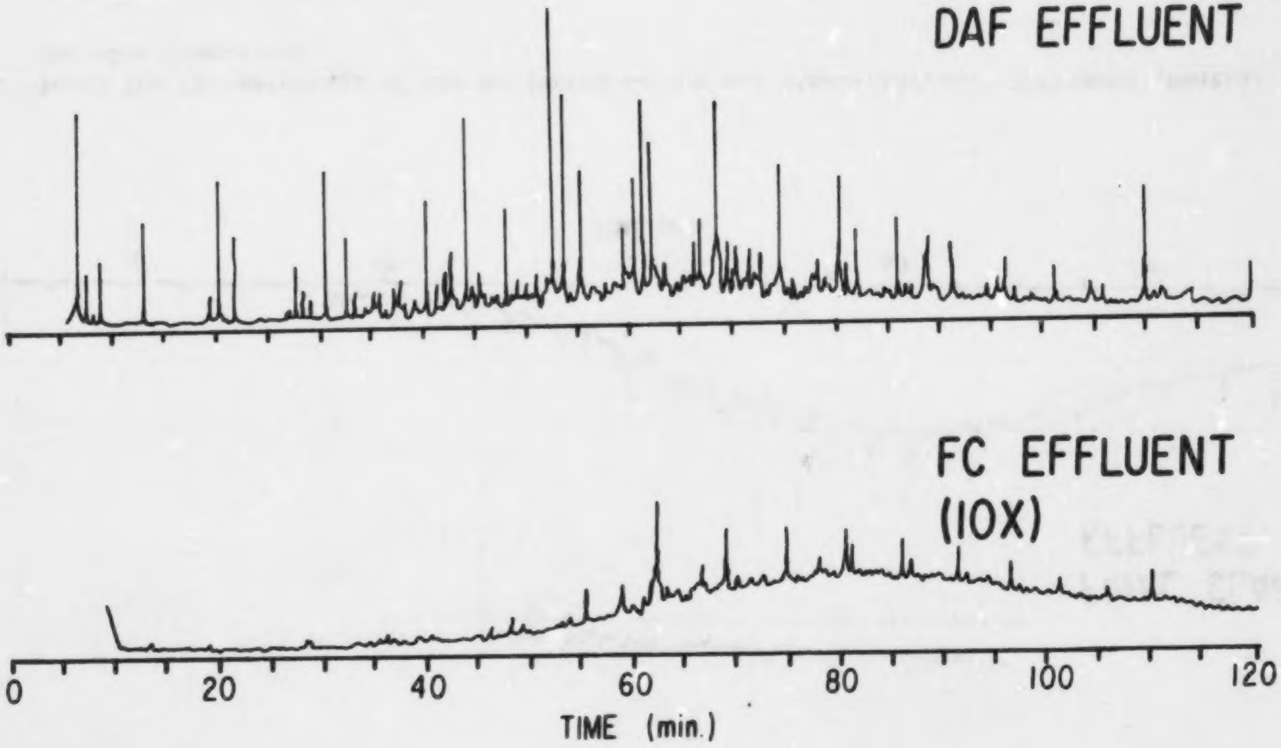


Figure 8. Total Ion Chromatograms of DAF Effluent and FC Effluent (Neutral Fraction, Four-Day Composite)

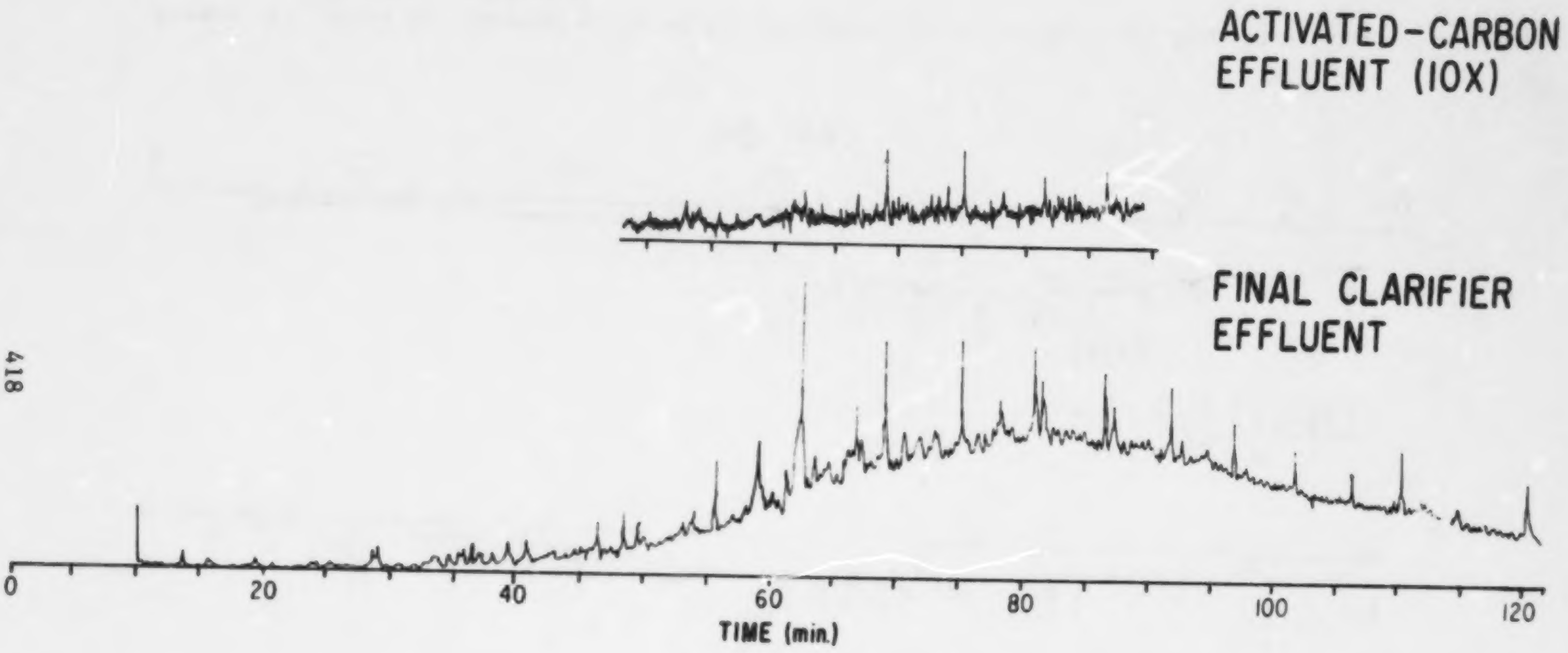


Figure 9. Total Ion Chromatograms of the Activated-Carbon and Final-Clarifier Effluents (Neutral Fraction, Four-Day Composite)

"GRANULAR CARBON REACTIVATION: STATE-OF-THE-ART"

R. H. Zanitsch
Engineering Director, Calgon Environmental Systems Division

R. T. Lynch
Process Engineer, Calgon Corporation

Use of granular activated carbon for treatment of industrial wastewater is receiving widespread acceptance. In the past several years, 100 adsorption systems have been installed in industrial plants. Applications range from dye plant wastewater reuse to removal of toxic materials. Granular carbon is being used to treat flows as low as 1,000 gallons per day to as high as 20,000,000 gallons per day in industrial waste applications. It is being employed as a pretreatment step to remove toxic materials prior to biological treatment, as the main treatment process and for tertiary treatment of biological plant effluents.

In most industrial wastewater applications, cost of virgin carbon prohibits using it on a throw-away basis. Chemical regeneration is feasible in only a limited number of applications and regenerant disposal remains a problem. Thermal reactivation is in most cases complete, efficient, and economical whether it is performed on-site or on a contract basis at a central reactivation facility.

The technology of reactivation with industrial waste carbons has developed in only the last ten years. There are now approximately twenty reactivation systems installed in the United States which are reactivating industrial wastewater carbons.

New thermal reactivation processes (such as fluidized beds and electric furnaces) are now being developed but no commercial experience with industrial wastewater carbons has been developed in the United States. For the purposes of this presentation, we will discuss our experience with the design and operation of multiple hearth furnaces and rotary kilns as they relate to industrial wastewater applications.

THE THERMAL REACTIVATION PROCESS

Granular carbon is usually wet when fed to the reactivation furnace. Water concentration is a function of carbon size, water temperature during the dewatering step, and the amount of adsorbate on the carbon. In practice, moisture content varies from 40 to 50 percent on a wet spent basis.

The reactivation process can be divided into three steps:

1. Evaporation of moisture on the carbon (Drying).

2. Destructive distillation of organics resulting in pyrolysis of a portion of the carbon from the organic materials (Baking).

3. Activation of the carbon by selectively burning carbon deposited during the organic removal step (Activation).

During the drying step, carbon temperature is increased to approximately 212°F (100°C) and moisture evaporates into the gas phase. As moisture evaporates it is also possible for highly volatile organics to be steam distilled.

The second step is termed baking or pyrolysis of the adsorbate. During this step, carbon temperature increases to approximately 1200-1400°F (649-760°C). A portion of the organic molecules are thermally cracked to produce gaseous hydrocarbons which are driven off. The remaining lower molecular weight organics are distilled. During this process, a carbon char is deposited in the pore structure of the original activated carbon.

The final step is activation of the carbon - a chemical reactivation whereby carbon char deposited during the baking step is combusted along with a small amount of the original carbon. By this time, temperatures are in the range of 1600-1800°F (871-982°C).

Since the fixed carbon and the granules are both carbon, the process requires that fixed carbon be selectively gasified with minimum gasification of the granular carbon. Steam is added to the furnace and oxygen concentration is controlled to promote gasification of the fixed carbon while minimizing burning of the original granular carbon.

REACTIVATION SYSTEM DESCRIPTION

The basic sequence for thermal reactivation is as follows: (See Exhibit 1).

Spent carbon is removed from the adsorbers and transferred as a slurry to a spent carbon storage tank. Spent carbon is then transferred to an elevated furnace feed tank from which it is metered, at a controlled rate, to a dewatering screw. The dewatering screw is an inclined screw conveyor which serves the dual purpose of gravity draining slurry water from the granular carbon and providing a water seal for the top of the furnace. A timer operated valve is used to meter carbon to the dewatering screw. Drained, but wet, spent carbon then gravity flows into the furnace where it is dried, baked, and reactivated as discussed earlier. Reactivated carbon exits the furnace by gravity and enters a quench tank. The quench tank serves the dual purpose of wetting the reactivated carbon and providing a bottom seal for the furnace. The carbon is then transferred to a reactivated carbon storage tank from which it is then returned to the adsorbers as needed. In most industrial waste applications, an afterburner and scrubber are provided for destroying organics and removing residual particulates from the furnace off-gases.

The spent carbon storage tank should be designed for five to ten days storage of carbon in order to allow for routine furnace maintenance and unscheduled shut-downs. This is usually a lined carbon steel tank with a cone bottom to facilitate carbon flow. The reactivated carbon storage tank is usually sized in the same manner with the same materials of construction. In the case of the reactivated carbon storage tank, facilities should be provided for adding virgin makeup carbon to the system as required.

The furnace feed tank is usually sized for at least one shift of operation. The feed tank insures a constant carbon feed to the furnace independent of the large storage system. This tank is usually a cone-bottom, lined carbon steel tank.

Spent and reactivated carbon are transferred in slurry form using either eductors, blowcases or slurry pumps. In the case of eductors and pumps, dilution water must be provided in order to reduce slurry concentration to less than one pound per gallon to minimize carbon abrasion and line erosion. Eductors are generally applicable in non-corrosive services where static head is not great. Pumps can be used satisfactorily in high-head applications, but are subject to erosion and plugging. Eductors and pumps require use of dilution water which necessitates installation of water recycle systems. The blowcase is an efficient method of transferring carbon. Both air and water have been used to pressurize blowcases. In the case of a blowcase, carbon is transferred in a much denser slurry (three pounds per gallon) and, therefore, care must be taken to maintain control over line velocities to minimize abrasion and wear. Material for carbon slurry lines should be compatible with the wastewater. As long as slurry lines are flushed free of carbon after each transfer, galvanic corrosion of carbon steel lines will not be a problem; however, if the wastewater is corrosive, more exotic materials of construction should be used. All carbon slurry lines should be equipped with flush connections to facilitate flushing and unplugging.

CAPITAL AND OPERATING COST ESTIMATES

Based on our experience with the design, installation, and operation of multiple hearth furnaces and rotary kilns for reactivating industrial waste carbons, we have estimated the installed cost of reactivation systems to reactivate 5,000, 10,000, 30,000, and 60,000 pounds per day. (See Exhibit 2). The capital cost curve shown in Exhibit 3 represents a total installed cost including all equipment, site preparation, foundations, installation, startup, and indirects. We have assumed that necessary utilities and off-site facilities are available at the battery limits. As you can see, we estimate the total installed cost of a 10,000 pound per day reactivation system to be approximately $1.25 million plus or minus 20 percent. The time required to design, procure, install, and startup a reactivation system is usually estimated to be two years assuming a twelve-month delivery time on the furnace and associated equipment.

We have also estimated direct operating costs for reactivating 5,000, 10,000, 30,000, and 60,000 pounds per day of industrial wastewater carbons as shown in Exhibit 4.

In order to develop these costs, the following elements were considered:

1. Labor was estimated to be one operator per shift at a rate of $10/hour. An allowance of 25 percent of the labor cost for supervision was also included.

2. Fuel was estimated at 8,000 BTU's per pound at a cost of $3/million BTU's. This estimate includes afterburner operation and an allowance for inefficiencies due to interruptions and reduced feed rates. Approximately half of the fuel consumption is required for the afterburner and idling.

3. Power costs for the reactivation system are minimal and were assumed to cost $0.03/KWH.

4. Steam costs were based on an average demand of one pound of steam per pound of carbon for reactivation at a cost of $4/1,000 pounds.

5. Maintenance costs for an industrial wastewater application can range from 8 to 15 percent of the reactivation system cost per year. For this estimate, we assumed a maintenance cost of 8 percent per year.

6. Makeup carbon costs were based on an average carbon loss rate of 7 percent and a virgin carbon cost of $0.57/pound delivered. Carbon losses can range from as low as 3 percent to greater than 10 percent depending on design and operation of the system. Most industrial waste systems operate in the 5 to 7 percent loss range. Makeup carbon costs represent the highest individual cost element in the direct operating cost estimate and, therefore, all efforts should be made to minimize carbon losses through good design and operation.

7. A general plant overhead of 10 percent of the above cost was allowed to cover such items as insurance, taxes, monitoring, accounting, and administration.

As can be seen from Exhibit 4, the direct operating cost for a reactivation system handling industrial wastewater carbons ranges from $0.11 to $0.19/pound over the range investigated. This does not include depreciation or amortization of investment. The economies of scale are obvious. We feel these costs can range plus or minus 20 percent, but in general, reflect the cost to operate a reactivation system on industrial waste applications.

MULTIPLE HEARTH FURNACE

Exhibit 5 is a cross-sectional view of a multiple hearth furnace. The furnace consists of a cylindrical refractory-lined steel shell containing several refractory hearths and a central rotating shaft to which rabble arms are attached. From four to eight hearths are used in carbon reactivation furnaces. The center shaft and rabble arms are cooled by air supplied by a centrifugal blower discharging air through a housing into the bottom of the shaft. A sand seal at the top of the furnace and a sand or water seal at the bottom are used to seal the furnace against introduction of extraneous air.

In operation, wet spent carbon is introduced through a chute into the outside of the top hearth of the furnace. The rabble arms are equipped with solid alloy rabble teeth which rake the carbon towards the center where it drops to the hearth below. The teeth on the rabble arms are arranged to move the carbon in a spiral path. The action is gentle to minimize attrition. The top hearth is termed an "in" hearth since carbon flow is inward.

The second hearth is consequently an "out" hearth where the carbon is moved outward by the rabble teeth. Out hearths have a series of holes around the periphery of the hearth through which the carbon drops to the next lower hearth.

In this manner, carbon passes through the furnace until it is finally discharged through a chute in the bottom hearth into the water filled quench tank. The chute extends under the water level in the quench tank to provide a seal.

Drying is accomplished in the upper one-third of the furnace. Distillation and pyrolysis of the adsorbate occurs in the next one-third. Activation of the carbon is completed in the bottom one-third of the furnace.

Burners are mounted tangentially on the furnace shell in burner boxes. Usually burners are placed on the bottom two or three hearths and on one upper hearth below the lowest drying hearth. However, if desired, burners can be mounted on any hearth including the drying hearths.

On small furnaces, two burners per fired hearth are used. On larger furnaces, three burners are installed. The burners are of the nozzle-mix type burning fuel oil or natural gas. Dual fuel burners are commonly employed to burn gas when it is available and fuel oil at other times.

Steam addition ports are provided on the bottom two or three hearths to add steam for control of the reactivation process.

The center shaft is driven through a variable speed drive at 0.5 to 2.5 rpm.

A number of furnaces have been installed with integral or "0" hearth afterburners. This is less costly from a capital cost standpoint than the separate afterburner.

DIRECT FIRED ROTARY KILN

Exhibit 6 is a simplified sketch showing a direct-fired rotary kiln. The kiln is a refractory lined steel shell enclosed on each end with refractory lined stationary hoods. This sketch depicts a counter-current operation where gas flow is opposite the carbon flow. Co-current operation is also possible and one carbon reactivation kiln is currently operating in this manner.

The kiln is mounted on two or three sets of trunions depending on the length of the unit. The kiln is sloped from the feed to the discharge end and one set of thrust rolls are used to maintain the kiln in position on the trunions. Proper training and alignment of trunions is important to minimize excessive wear of the trunions and tires.

The kiln is driven through a variable speed drive coupled to a speed reducer and pinion gear which meshes with a bull or girt gear mounted on the kiln shell. The kiln is equipped at each end with hoods. Rotary seals are used to seal between the rotating kiln shell and the stationary hoods. The hoods are refractory lined.

A feed screw or chute is used to feed wet carbon into the kiln. Flights are usually employed to advance the damp carbon and to shower the carbon in the feed end to obtain high heat transfer rates during the evaporation step. Flights are also used in the first portion of the baking step up to a point where the temperature reaches approximately 1200-1400°F (649-760°C). Material of construction for the flights is a function of carbon corrosiveness and reactivation conditions in the kiln.

The hot reactivated carbon, at a temperature of 1600-1800°F (871-982°C), discharges from the kiln and falls down the discharge chute into a water-filled quench tank. The discharge chute extends under the water level in the quench tank to form a seal to eliminate air leakage into the kiln.

A burner is mounted in the discharge hood to provide heat for the reactivation process. Either fuel oil or gas may be burned. The burner air-to-gas ratio is adjusted to minimize oxygen concentration in the kiln. A steam addition port also is provided in the discharge hood to admit steam into the kiln for control of the reactivation process.

The exhaust gases, at a temperature of 500-800°F (260-427°C), leave the kiln through a duct connected to the feed hood. In most installations, gases are passed through an afterburner for complete combustion of organics and burning of carbon fines swept out of the kiln. New installations, as is the case with the multiple hearth furnace, will probably require installation of a wet scrubber to meet air pollution codes in most areas of the country.

In a rotary kiln, reactivation process is controlled by varying the kiln speed to provide adequate retention time and by adjusting the steam rate and burner temperature at the settings required for the particular carbon to be reactivated. A steam rate of 0.6-1.2 pounds per pound of carbon and a temperature of 1600-2000°F (871-1093°C) are ranges encountered in practice.

OPERATING AND MAINTENANCE PROBLEMS

A number of unique operating and maintenance problems have been experienced in reactivating industrial wastewater carbons. These problems include:

Corrosion
Slagging
Poor Reactivated Carbon Quality
High Carbon Losses
Feed Interruptions
Hearth Failures
Slurry Line Erosion and Corrosion

Corrosion

Selection of proper construction materials for carbon storage and handling systems is very important. We have found lined carbon steel tanks to be satisfactory, but proper selection and application of lining material is extremely important. Lining material should be corrosion and abrasion resistant. We recommend thorough corrosion coupon testing prior to making a final selection. Erosion of lining material at carbon outlet nozzles, followed by corrosion of the metal, has been a problem. We have installed sacrificial wear plates or stainless steel cones on tanks in order to minimize this problem. Dewatering screws and quench tanks are generally constructed of 304 or 316L stainless steel. In general, these materials are satisfactory for most applications. However, the dewatering screw is exposed to the spent carbon slurry and, therefore, its material must be compatible with the wastewater. Corrosion of rabble arms and teeth in multiple hearth furnaces and lifting and drying flights in rotary kilns can be a problem when handling chlorinated hydrocarbons and organic sulfur compounds. Special attention must be given to material selection to minimize this problem.

Slagging

Formation of clinkers and slag in the furnace is generally a function of sodium and/or organic phosphate content of the spent carbon. Slag formation can be minimized by pretreatment of carbon and maintenance of proper furnace conditions. Formation of slag can generally be attributed to constituents in the water contained in the pores of the carbon as it enters the furnace. These chemicals react with alumina and silica in the furnace refractory resulting in slag formation.

Hearth Failures

Hearth failures in multiple hearth furnaces can generally be attributed to cyclic operation. Frequent feed interruptions, resulting in temperature excursions on the upper hearths, will weaken hearths and ultimately lead to failure. By minimizing the number of feed interruptions and maintaining continuous furnace operation, upper hearth life can be maintained for three to five years. Another problem leading to hearth failure is brick attack by sodium compounds; which leads to the slagging problem discussed earlier. Also, improper dewatering or improper operation of the dewatering screw, which would result in excessive amounts of water entering the top hearth, can result in thermal shock which leads to failure. In general, hearth life is a function of the operating philosophy of the furnace. If frequent feed interruptions due to improper carbon feed system design or cyclic operation are encountered, poor hearth life can be expected.

Carbon Losses

As mentioned earlier, makeup carbon cost is the single most important cost element for a reactivation facility. By properly designing the adsorbers, the carbon transfer and handling systems and the carbon storage and reactivation systems, losses can be controlled at the 5-7 percent level. Within the reactivation furnace itself, carbon losses should not exceed 1-3 percent. Carbon which is lost is due to oxidation during the activation step. This can be controlled by maintaining oxygen levels in the activation zone at 0-2 percent, or roughly that required for destruction of organics without sacrificing carbon. Most carbon losses in a granular carbon system occur due to backwashing of carbon in adsorbers, abrasion in slurry lines, spillage, and carryover in overflow lines. These losses can all be minimized by proper design of the basic system. Care must be given to overflow rates, backwash rates, and slurry line velocities, and frequent checks must be made to see that good housekeeping and operating techniques are being followed.

Slurry Line Erosion and Corrosion

As mentioned earlier, construction material of spent carbon slurry lines should be compatible with the wastewater in order to minimize corrosion. If spent carbon or reactivated carbon is allowed to accumulate in a carbon steel slurry line, galvanic corrosion can be expected. Therefore, flushing of all slurry lines after each transfer is recommended. If the wastewater is extremely corrosive, we recommend lined steel or stainless steel slurry piping be considered.

Erosion of slurry lines can be attributed to excessive transfer velocities. We recommend a slurry line velocity of 3-5 feet per second which is sufficient to prevent settling and minimize abrasion. Also, slurry lines should be as direct as possible with a minimum number of bends. We recommend that long-radius bends be used to minimize abrasion. Also, we recommend that all bends be accessible for periodic inspection and replacement. Flush connections should be provided at frequent intervals on all slurry lines in case a line becomes plugged.

FURNACE SELECTION CRITERIA

Choice of a reactivation furnace depends on many factors. A thorough analysis of each type of equipment plus reactivation characteristics of the carbon are necessary to make a final decision on which piece of equipment to use.

Both multiple hearth furnaces and kilns are being employed to reactivate granular activated carbon used in industrial wastewater treatment. The quality of reactivated carbon that can be achieved is the same for both units.

Major parameters influencing the selection of a reactivation furnace are as follows:

1. Capital Cost - Total installed costs for either a multiple hearth furnace or a rotary kiln are approximately the same. The purchase price is generally higher for a multiple hearth furnace. However, the installation costs are lower which tends to make installed costs the same. Site preparation, foundations, and structural costs are higher for a rotary kiln because of the greater area required to install a kiln.

2. Area Requirements - Area requirements are much greater for a rotary kiln than for a multiple hearth furnace. The kiln also requires more foundations and structural steel for walkways than a multiple hearth furnace. The multiple hearth furnace is higher than a kiln which means more structural steel is required to support the carbon feed equipment.

3. Fuel Consumption - Fuel consumption is higher in a rotary kiln because of higher heat losses. In a multiple hearth furnace, insulation is used behind the wall brick to minimize heat loss. This is not possible in a rotary kiln. Surface area is also higher in a rotary kiln than a multiple hearth furnace of equivalent capacity. Fuel consumption for each will be in the following ranges depending on capacity and operating rate as a fraction of rated capacity.

	BTU/LB Carbon*
Multiple Hearth Furnace	2500-4500
Rotary Kiln	3500-8000

*Does not include afterburner fuel requirements.

4. Capacity Turndown - Capacity turndown ratio is defined as the percent of rated capacity at which the furnace can be operated while producing good reactivated carbon with reasonable carbon loss. Capacity turndown for the equipment being evaluated in this paper are as follows:

Multiple Hearth Furnace	- 33 Percent
Rotary Kiln	- 50 Percent

The multiple hearth furnace can be operated at a lower fractional capacity because of the greater degree of control that can be obtained in various zones of the furnace. In a rotary kiln, with only one burner and one steam addition point, kiln speed is the major parameter that can be varied to operate at lower capacities.

5. Degree of Control - Better reactivation process control can be achieved in a multiple hearth furnace because the furnace is divided into distinct zones according to the number of hearths in the furnace. Each hearth can be equipped with burners, steam addition, and air addition which can be controlled independently. Thus, it is possible to control temperature and vary the atmosphere in each hearth to optimize carbon reactivation.

In a rotary kiln, the steam port, and burner can only be mounted in the firing end of the kiln. With this arrangement, the degree of control that can be achieved is less than in a multiple hearth furnace. In a properly sized kiln, this is not a distinct disadvantage and good carbon reactivation can be achieved. However, as discussed previously, capacity turndown is not as great in a kiln.

6. Corrosion and Slag - Many industrial waste streams contain inorganic impurities which can cause corrosion and slag formation in the reactivation furnace. These impurities are mostly chloride and sulfur salts of calcium and sodium. The multiple hearth furnace has more exposed alloy parts than a kiln and is, therefore, more susceptible to corrosion. Rabble teeth and arms are expensive, long delivery castings as opposed to the alloy flights in a kiln which are fabricated from readily available plates. Also, considerable corrosion of flights can occur in a kiln before replacement is required.

Slag buildup in a multiple hearth furnace will require periodic shutdowns to remove accumulated material. Slag in a rotary kiln will be discharged, with the reactivated carbon, into the quench tank where it can be removed without shutting down the process.

7. Maintenance - Experience with reactivating industrial wastewater carbons indicates higher maintenance costs in a multiple hearth furnace. The factors responsible are:

   a. Corrosion and slag formation resulting in shutdowns for repairs.

   b. Rabble teeth and arms are more expensive to replace than alloy flights used in a rotary kiln.

   c. Multiple hearth furnaces are more difficult to work on. It takes more man-hours to rebuild a hearth than to replace brick in a kiln. Because of these factors, downtime to affect repairs is longer in the multiple hearth furnace.

   d. More instrument components are required with a multiple hearth furnace.

8. Effect of Feed Outages - The upper hearths in a multiple hearth furnace can be damaged from temperature cycling caused by interruptions in furnace feed. Periodic planned shutdowns can be conducted without hearth damage.

   Feed outages are usually not a major problem in a rotary kiln. The refractory is much less effected by temperature cycling in a kiln than the hearth refractory in a multiple hearth furnace.

9. Operating Factors - Operating factors for kilns and multiple hearth furnaces are as follows:

Rotary Kiln	85-95 Percent
Multiple Hearth Furnace	75-90 Percent

   Multiple hearth furnaces must be shutdown more often to clean slag and replace rabble teeth. When a furnace is down for repairs, the work requires more man-hours to complete than similar work on a rotary kiln.

   Based on the above parameters, the multiple hearth furnace offers the following advantages over a rotary kiln:

   - Better control of temperature and atmosphere
   - Lower fuel consumption
   - Greater capacity turndown

- Less area required
- Lower carbon losses from carryover and attrition

The rotary kiln advantages are:

- Less corrosion and slag formation
- Less downtime
- Lower maintenance costs and easier maintenance
- Less effect from feed outages
- Easier to operate

SUMMARY AND CONCLUSIONS

Granular activated carbon has been demonstrated to be effective in treatment of a wide variety of industrial wastewaters. Both multiple hearth furnace and rotary kilns can satisfactorily reactivate spent carbons used in industrial wastewaters provided adequate consideration is given to selection of materials, sizing of equipment, and operating philosophy. Experience gained over the last ten years indicates that corrosion, slagging, poor reactivation quality, carbon losses and line erosion can all be minimized through good design. Although the same types of problems exist in industrial purification and municipal water and waste treatment applications using granular activated carbon, they are magnified in industrial wastewater applications where wastewater quality, and thus carbon exhaustion rates, are more variable and substantially more corrosive. However, our experience with reactivating over 100,000,000 pounds of spent carbon for more than 75 different industrial wastewater applications, indicates that a high quality product can be produced on a reliable, economical basis.

BIOGRAPHIES

Roger H. Zanitsch is Engineering Director of the Calgon Environmental Systems Division for Calgon Corporation. He joined Calgon as a Project Engineer in 1969 and was later named Project Manager of the Environmental Engineering Department. Zanitsch received his BS degree in Civil Engineering from the University of Cincinnati and an MS degree in Environmental Engineering from the same school. Zanitsch is a member of the Water Pollution Control Federation.

Richard T. Lynch is a senior engineer in the Process Engineering Group of Calgon Corporation's Engineering Department. He has a B.S. degree in Chemical Engineering from the University of Florida. He has been a project manager for the design of several carbon adsorption reaction systems treating industrial waste streams. He is a member of the American Institute of Chemical Engineers and a registered professional engineer in Florida.

EXHIBIT 1

TYPICAL REACTIVATION SYSTEM FLOW DIAGRAM

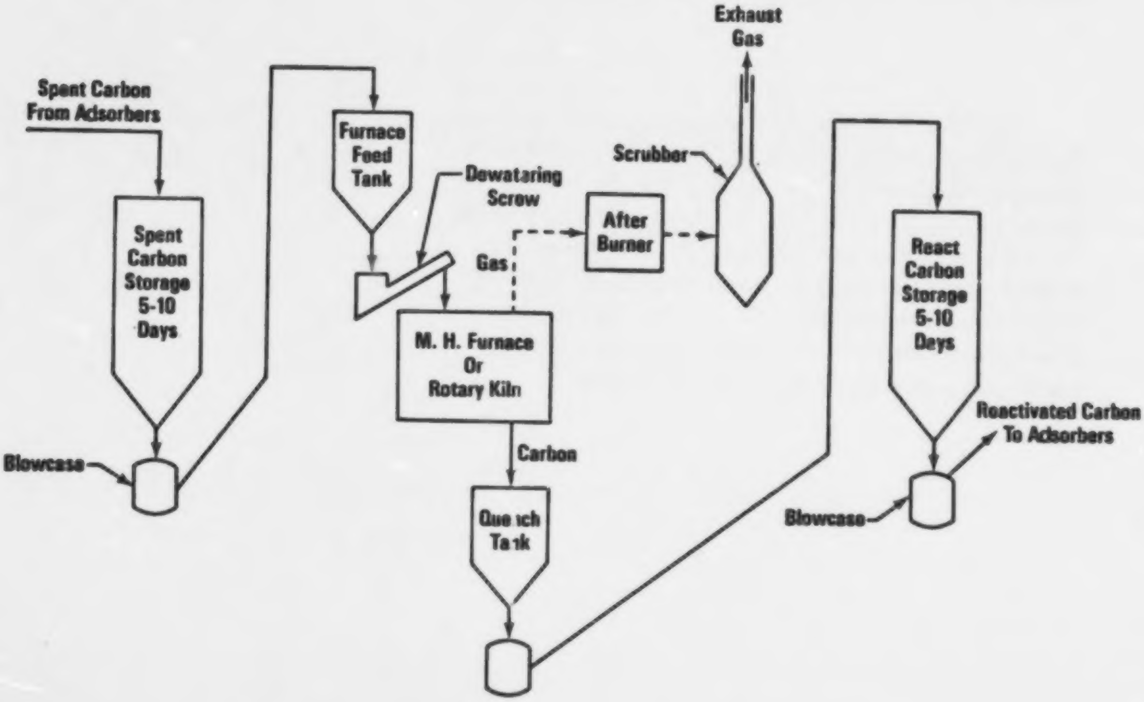

Exhaust Gas
Spent Carbon From Adsorbers
Furnace Feed Tank
Dewatering Screw
Scrubber
After Burner
Gas
Spent Carbon Storage 5-10 Days
M. H. Furnace Or Rotary Kiln
React Carbon Storage 5-10 Days
Reactivated Carbon To Adsorbers
Carbon
Blowcase
Quench Tank
Blowcase

EXHIBIT 2

INSTALLED COSTS OF REACTIVATION SYSTEMS

CAPITAL COSTS

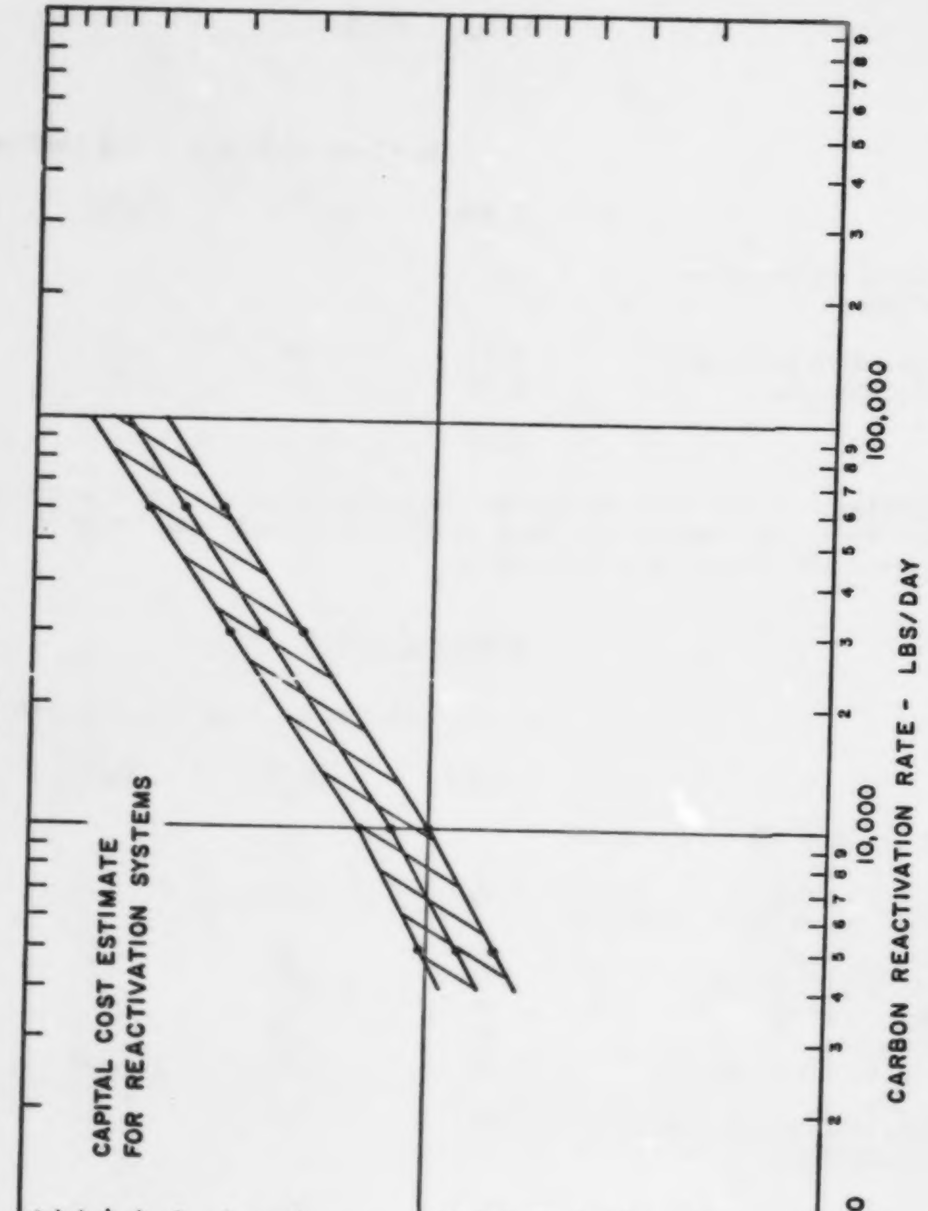
	Reactivation Rate - 1,000 Lbs/Day			
	5,000	10,000	30,000	60,000
Capital Cost Estimate ($ Million)				
Purchased Equipment	0.24	0.36	0.77	1.20
Installation*	0.61	0.91	1.93	3.00
	0.85	1.27	2.70	4.20

*Installation costs include foundations, structural equipment setting, electrical, instrumentation, site preparation, engineering contractor, overhead and profit, and indirects.

OPERATING COSTS

	Reactivation Rate - 1,000 Lbs/Day			
	5,000	10,000	30,000	60,000
Fuel - 8,000 BTU/Lb @ $3/10^6 BTU	45	90	265	525
Power @ 3¢/KWH	10	20	50	80
Steam - 1.0 Lb/Lb @ $4/1,000 Lbs	10	15	45	90
Labor @ Supervision	110	110	110	110
Makeup Carbon - 7% @ 57¢/Lb	70	145	435	875
Maintenance @ 8% Capital	70	100	215	335
General Plant Overhead	30	50	110	200
Total Operating Cost ($1,000/Yr.)	345	530	1,230	2,215
Operating Cost ¢/Lb Carbon	18.8	14.5	12.2	11.0

EXHIBIT - 3



CAPITAL COST ESTIMATE FOR REACTIVATION SYSTEMS

EXHIBIT - 4

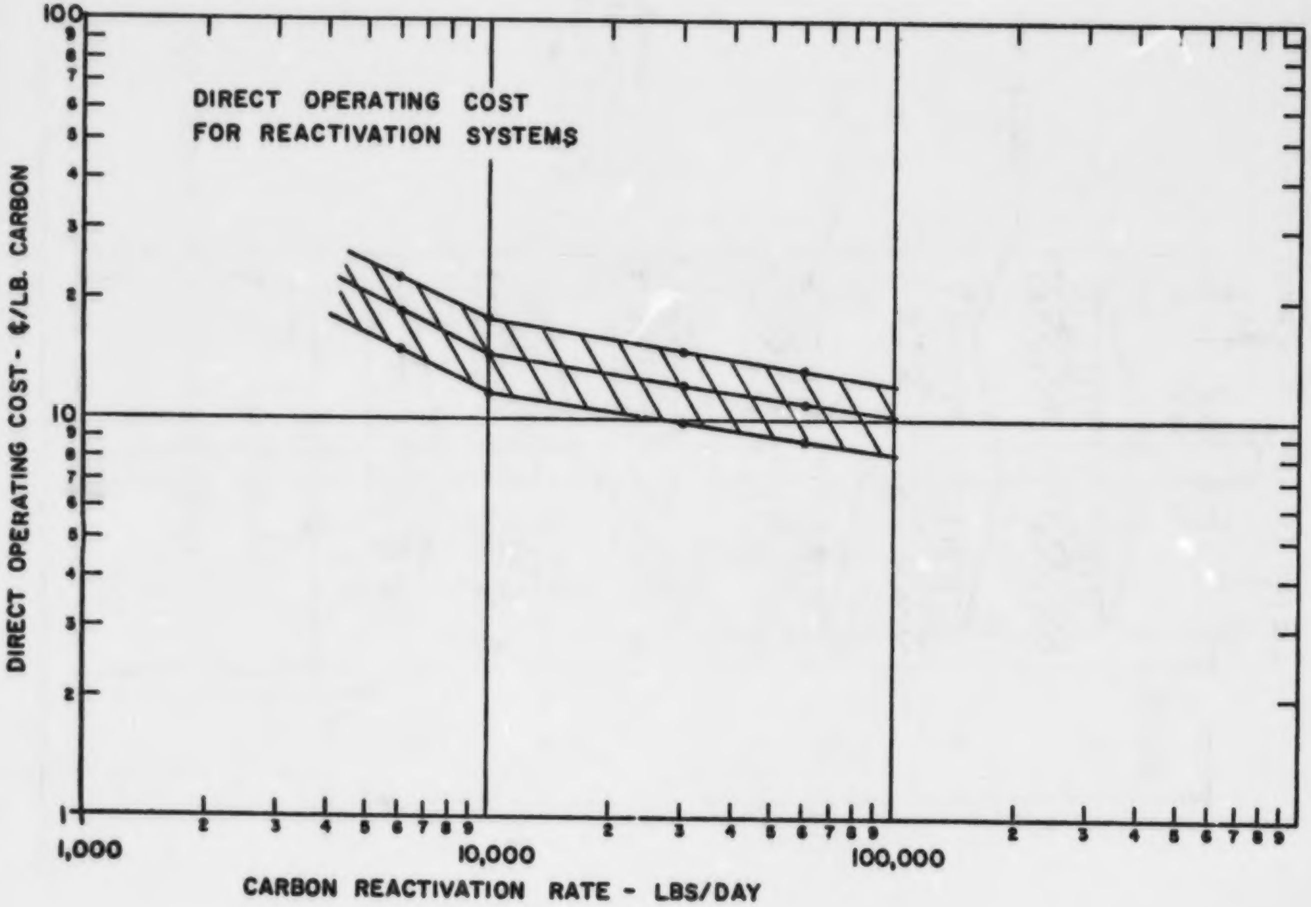

DIRECT OPERATING COST
FOR REACTIVATION SYSTEMS
DIRECT OPERATING COST - $/LB. CARBON
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
1,000
2
3
4
5
6
7
8
9
10,000
2
3
4
5
6
7
8
9
100,000
2
3
4
5
6
7
8
9
CARBON REACTIVATION RATE - LBS/DAY

EXHIBIT 5

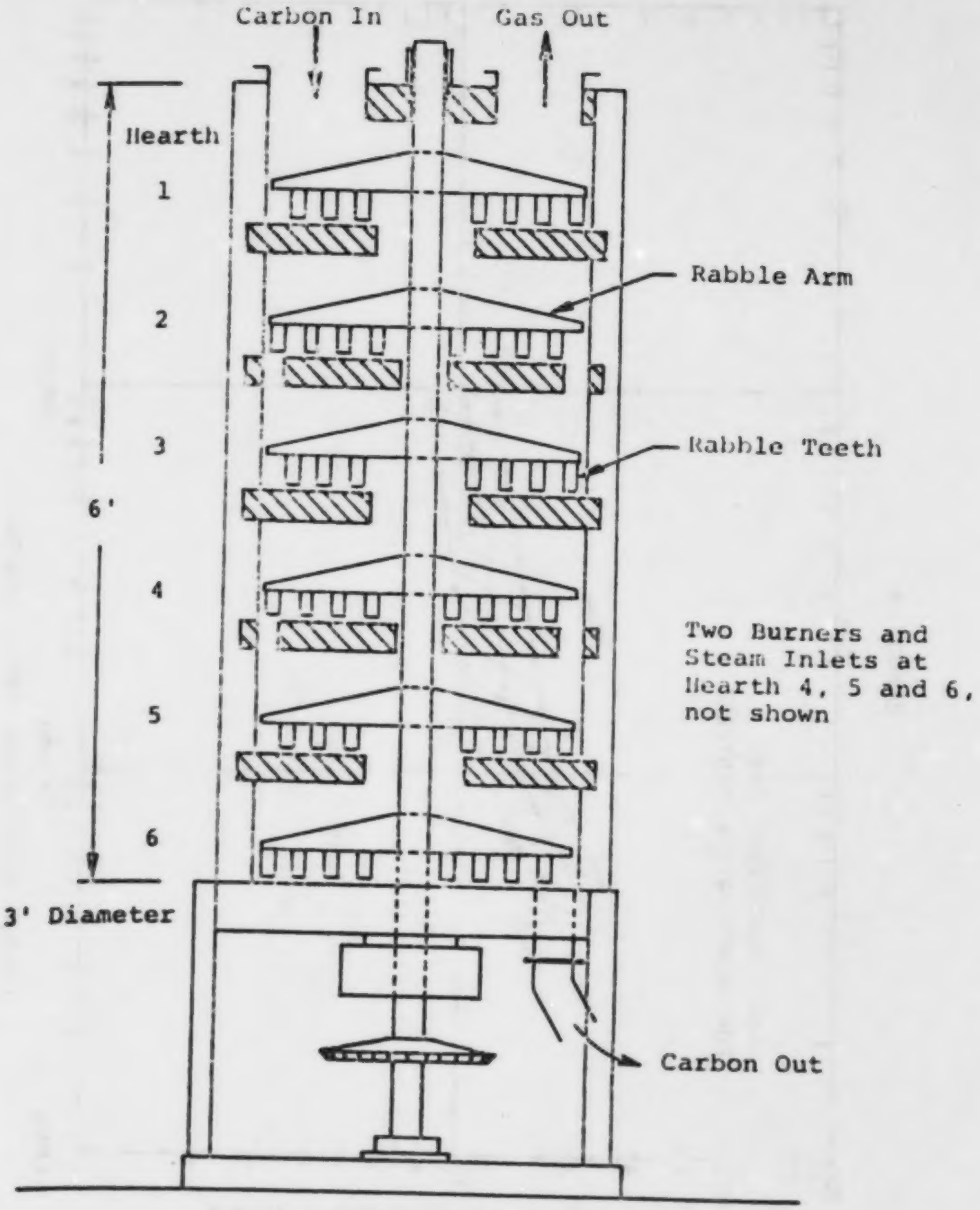
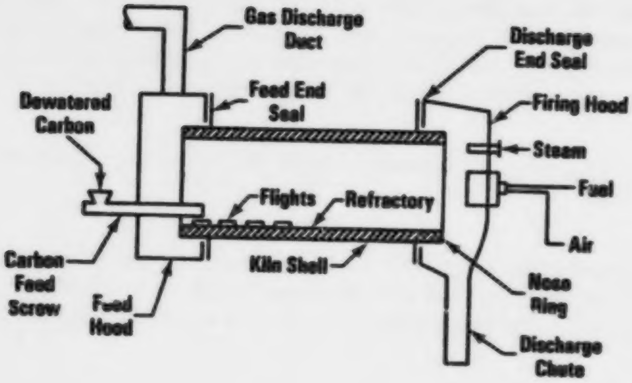


FIGURE 5 - CROSS SECTIONAL VIEW OF MULTIPLE HEARTH FURNACE USED AT POMONA WATER RECLAMATION PLANT

EXHIBIT 6


Gas Discharge Duct
Discharge End Seal
Feed End Seal
Firing Hood
Dewatered Carbon
Steam
Fuel
Flights
Refractory
Air
Carbon Feed Screw
Kiln Shell
Nose Ring
Feed Hood
Discharge Chute

DISCUSSION

L. L. Krohn, Union Oil Co.: Have you made an analysis of the off-gases from that furnace?

Roger Zanitsch: Yes, we have. We've looked at in excess of 100 different industrial waste carbons. We've analyzed the off-gases before and after afterburning on many of these, to determine what temperature and residence time is needed for organic destruction.

L. L. Krohn, Union Oil Co.: Do you have any feel for the particulate matter coming out?

Roger Zanitsch: We have systems operating that are designed with a 2 second residence time which is primarily there to consume the particulates. If you have a half second residence time which is certainly sufficient to destroy most of the organics present, you'll still have some carbon fines that will need to be scrubbed. We feel that the 1-2 second residence time at 1800°F can destroy the carbon fines as well as the organics.

L. L. Krohn, Union Oil Co.: Considering the new source review - can we hope to build this system?

Roger Zanitsch: Reactivation furnaces are now in operation and many are being designed for industrial waste applications. Technology exists to handle essentially all air pollution control requirements at a reasonable cost.

Mac McGinnis, Shirco, Inc.: We have made some of the economics that you're talking about for our electric regeneration furnace and compared them with similar economics as you have presented here from multiple hearth and other approaches and just a couple of comments - a couple of factors that we have included that you haven't mentioned are in the area of utilities, scrubber water which on small capacity units may be a fairly significant contribution of operating costs; and the other factor you mentioned quality of the product, laboratory labor, lab time to confirm that the product is indeed of the desired quality, can be a fairly significant contribution.

Roger Zanitsch: I'm glad you brought this up. In the analysis that I showed, the operating cost included a 10% general plant service allowance on the total operating cost to cover overhead items such as accounting, quality control, etc. As far as scrubber water cost and disposal, it can be a factor. In those installations where we have scrubbers, we've recycled water through the pretreatment system to remove the carbon fines. Frankly, we haven't found this to be a significant cost factor.

DISCUSSION

Mac McGinnis, Shirco, Inc.: Well, a half cent here and half cent there, it begins to add up. The other general comment is you've indicated that there is considerable data on regeneration costs in multiple hearth furnaces in particular and you've showed us some trend lines in terms of direct operating costs. Can you comment on any specific data, you know, accumulated over a period of time that indicates an actual cost figure for some specific application?

Roger Zanitsch: The numbers which I presented are based on our experience in operating both small and large furnaces.

Mac McGinnis, Shirco, Inc.: One last comment - would you say then that the actual data would fall within that plus or minus 20% about your nominal curve?

Roger Zanitsch: On industrial waste applications, yes. In process applications, such as the decolorization of sugar solutions, operating costs are substantially lower since they have a constant feed and a very predictable product.

Colin Grieves, Amoco Oil Co.: First, would you care to comment on some of the new technology which you eluded to? And second, would you like to say anything about regeneration of powdered activated carbon?

Roger Zanitsch: As far as the new technologies are concerned, I was personally thinking of the electric furnace and the fluidized bed furnaces. The Japanese have several different types of furnaces. Most of the experience with the newer furnaces has been in either pilot-scale or on the commercial scale, but in considerably less corrosive application than you have in industrial wastes. In industrial waste applications, the big awakening has been in the areas of corrosion, maintenance costs, and feed interruptions. The new technologies have not been demonstrated in this type of service. As the new technology develops, it's going to take some time to gain the experience necessary to apply these new furnaces in the industrial waste effort. As far as powdered carbon activation, I don't really feel qualified to discuss it on the basis that I would only be expressing my opinions since no commercial experience has been developed.

"ACTIVATED SLUDGE ENHANCEMENT: A VIABLE ALTERNATIVE TO TERTIARY CARBON ADSORPTION"

Leonard W. Crame

Senior Chemical Engineer, Texaco Inc.

INTRODUCTION

In view of the possibility of more stringent 1983 BATEA (Best Available Technology Economically Achievable) effluent guidelines,[1,2,3,4] petroleum refiners are faced with the dilemma of an insufficient data base to determine the proper approach for making cost-effective improvements. The EPA previously proposed granular activated carbon adsorption after activated sludge treatment as BATEA technology; however, the current emphasis is to consider both effluent quality and the cost effectiveness of attaining the desired results. Two proposed approaches to BATEA technology are (1) increasing the sludge age (or mean cell residence time) of the activated sludge biomass to develop a more diverse population capable of assimilating biorefractory organics or (2) adding powdered carbon directly to activated sludge aeration basins. Both alternatives to tertiary carbon adsorption would require little capital investment and would lower operating costs.

Grutsch and Mallatt[5,6,7,8,9,10,11] have proposed that the best refinery end-of-pipe treatment for soluble organic removal should include pH control, equalization, optimized dissolved air flotation (DAF), and high sludge age (20-50 days) activated sludge treatment. High sludge ages (SA) require mixed liquor solids levels above conventional levels (5-10 days SA). These higher levels increase solids flux and must be considered in secondary clarifier solids loadings. Also high effluent TSS, despite less frequent sludge wasting, can result in a loss of mixed liquor solids.

Grutsch and Mallatt emphasize that optimized chemically-assisted DAF pretreatment (or comparable pretreatment) reduces the colloid charge (zeta potential) to maximize particle agglomeration for efficient flotation, and reduces the organic load on the activated sludge unit (ASU). Removing colloids normally present in raw refinery wastewater allows better bioflocculation and lower effluent total suspended solids (TSS) since most refinery colloids and biosolids have repelling negative charges. The microbial population could then acclimate to the biorefractory organics by producing enzymes which reduce these to simpler biodegradable substrates. Current reports from within the petroleum industry seem to indicate some benefits for increasing SA. Other investigators[12] have reported that high SA (low food/microorganism ratio) produces poor sludge settleability.

As a result of pilot studies at the Du Pont Chambers Works, Hutton and Robertaccio[13] were issued a U.S. patent[14] for the Du Pont PACT process.[15] The PACT process basically involves the addition of powdered carbon (or fuller's earth, etc.) to an ASU, usually in a range of 50-400 mg/l based on influent flow. Du Pont has reported[16,17,18] a number of advantages of the PACT process which include:

(1) color removal,
(2) stability against shock loadings,
(3) improved BOD removal,
(4) improved refractory organic removal,
(5) resistance to toxic substances,
(6) improvement in hydraulic capacity,
(7) improved nitrification (mainly in municipal wastes),
(8) foam suppression, and
(9) improved sludge settling and increased clarifier capacity.

A disadvantage of the PACT process is that the system can become very expensive if powdered carbon addition rates become high (hundreds of mg/l), even though powdered carbon is cheaper than granular carbon.

DeJohn and Adams[19,20,21] have developed a considerable amount of pilot study data on activated sludge-powdered carbon systems. They report significant enhancement in studies involving refinery and petrochemical wastewaters. DeJohn and Adams explain the powdered carbon enhancement mechanism as localization and concentration of oxygen and pollutant as the result of adsorption on carbon surfaces, resulting in a more complete biooxidation. The adsorption of biorefractory organics allows a longer residence time for these components in the system. Other researchers[22,23] have found similar improvements using activated sludge-powdered carbon systems and propose analogous enhancement mechanisms.

Rizzo[24] has reported a case history of a full-scale activated sludge-powdered carbon demonstration run at the Corpus Christi, Texas, Sun Oil refinery. Results included better system stability, reduction of foaming, resistance to upset conditions, lower effluent suspended solids and clearer effluent, and improved organic removal. These improvements were achieved by maintaining only a 450-mg/l powdered carbon reactor concentration with a 10-mg/l powdered carbon dosing requirement. The shortcoming of this investigation was that a parallel control could not be run simultaneously and most improvements reported could possibly have been attributed to better clarification.

The merits of powdered carbon enhancement have been further confused with the more recent development of several types of powdered carbons with significantly different properties.

SCOPE OF WORK

1. Objective

The objective of this study was to determine if the relatively simple process changes of increased sludge age or the addition of powdered activated carbon in conventional refinery activated sludge systems can significantly enhance the removal of organic wastewater contaminants to achieve or approach the level of proposed BATEA (1983) technology more cost effectively than the addition of granular activated carbon contactors to BPCTCA (1977) technology.

2. Procedures

In Part I of this study, five completely-mixed (15 gal) ASU's were operated in parallel with identical 18-hr retention times and 300-gpd/sq ft clarifier rise rates. A sixth ASU was run as a second-stage unit with the same 18-hr retention time (Figure 1). All biological reactors were located in a temperature controlled room in an attempt to dampen influent wastewater temperature variations and control biological reactions at about 85 F.

ASU's A and F served as controls, simulating conventional refinery units with a 0.3 lb TOC/lb MLVSS-day organic loading. Separate controls were run to determine the effect of optimized pretreatment on activated sludge treatment and tertiary carbon adsorption. Equalized (24-hr) and pH-controlled refinery wastewater was pretreated by dual-media (sand-anthracite) filtration (4.6 gpm/sq ft) and a chemically assisted DAF unit (1.5 gpm/sq ft) prior to control ASU's A and F, respectively. The optimized DAF pretreatment neutralized the negatively charged colloids, thus facilitating their removal and producing a bio-unit feed that contained essentially only soluble organics. Sodium phosphate (monobasic) was added to the filter and DAF unit effluents for a minimum TOC:phosphorus ratio of 100:2 to assure a proper nutrient level. Effluents from ASU's A and F were continuously filtered through a dual-media (sand-anthracite) tertiary filter for TSS removal before passing through a series of four granular activated carbon contactors to simulate proposed 1983 BATEA technology.

ASU's B, C, and D treated optimized DAF effluent with sludge wasting calculated for a 50-day biological SA. A commercially available, conventional-surface-area, powdered carbon[25] (designated PC-C) was added daily to ASU C to maintain a 500-mg/l reactor operating level. Similarly, PC-H, a high-surface-area powdered carbon,[26] was added to ASU D to investigate its enhancement capabilities.

ASU E was also operated at a 50-day SA treating ASU B effluent to determine if there was any benefit to ASU staging.

In Part II of this study, the second-stage ASU E was placed in parallel with other ASU's treating the DAF unit effluent as shown in Figure 1 and redesignated as ASU G. PC-H was added to ASU G to maintain a 2500-mg/l operating level while powdered carbon levels were increased in ASU C and D to 1000 mg/l.

Effluents were collected daily, Monday through Friday, as grab samples. Grab samples were taken in lieu of composites for convenience since the pilot unit treatment scheme contained significant equalization. Samples from the equalization basin, biological reactors, and carbon columns were filtered with Gelman type A/E glass fiber filters to give the soluble contaminant (TOC, COD, S=) level. Glass fiber filters were used instead of 0.45-micron filters because the solids retained on glass fiber filters define the TSS measurement. Samples were analyzed immediately after collection or were preserved until analyzed using accepted preservation methods.[27]

All effluent data were compared after plotting values on log-normal probability papers. Single straight line data fits were determined by calculating 50th and 90th percentile values. The 50th percentile values equaled the antilog of the mean of the log values of data sets. The 90th percentile values were calculated assuming a single-tailed log-normal data distribution

$$\ln N_{90} = \ln N_{50} + 1.282 \ln S_d$$

where

S_d is the standard deviation.

Engineering judgment was used to determine which data sets being compared appeared different and required additional statistical analyses to confirm significance of median differences. Median data values were compared to determine if they were from the same population using a paired t-test[28] assuming a log-normal distribution as follows:

$$\text{compute } t = \frac{\bar{d}}{\sqrt{\dfrac{\Sigma d^2 - (\Sigma d)^2/n}{n(n-1)}}} = \frac{\bar{d}}{\sqrt{S_d^2/n}}$$

$$\bar{d} = \text{mean of differences} = \sum_{1}^{n} d_i/n \text{ where } d_i = \ln x_i - \ln y_i$$

for $i = 1,2,3,.,.n$ of n data pairs

S_d = standard deviation of d_i.

The test hypothesis is that data are from the same population, therefore, their true medians are equal. This hypothesis is rejected if the calculated t-value exceeds the tabled two-tailed t-value for n-1 degrees of freedom for the selected (90 percent) confidence level.

RESULTS

1. Part I - Pretreatment

The blended refinery wastewater contained excessive amounts of colloids and TSS coated with oil, complicating pretreatment. The DAF unit chemical dosages were relatively high at 40 mg/l filter alum ($Al_2(SO_4)_3 \cdot 14.3$

H_2O) and 20-40 mg/l Dearborn 431 cationic polymer. Chemical dosages were initially optimized using zeta potential titrations in conjunction with jar tests; however, only jar tests were continued since zeta potential calculations became tedious and inconsistent due to the high wastewater specific conductivity (usually 4000-8000 micromhos/cm). This salinity was primarily due to the brackish intake waters to the refinery and may have impeded chemical coagulation at lower chemical dosages as reported by Grutsch and Mallatt.[8]

The superiority of the optimized DAF unit (operating at 1.5 gpm/sq ft) as a pretreatment system over simple sand filtration is clearly evident in the three weeks of run data represented in Figure 2.

DAF unit effluent 50th percentile TOC (158 mg/l) was 55 percent less than the 50th percentile TOC (352 mg/l) in the equalization basin influent to the DAF unit, while the sand filter gave only a 18-percent reduction. Since, at best, only a 31-percent TOC reduction could be achieved by vacuum filtration of equalization basin samples with glass fiber filters (which define TSS), the true effectiveness (55 percent reduction) of colloid and oil coagulation and removal in the chemically assisted DAF unit can be seen. The DAF unit effluent contained essentially only soluble organic contaminants.

The continuous dual-media filter (operating at 4.6 gpm/sq ft) could only manage a TOC reduction of about one-third of the DAF unit. There was no indication that a shorter run time would improve the filter effluent significantly. It appeared that due to the nature of the solids, chemical addition to the filter feed would have been required for an improved system. The purpose of the filter, however, was to produce a biological reactor feed with characteristics comparable to DAF treatment without chemicals. It was observed, on occasions, that DAF pretreatment was very poor when chemical feed pumps failed.

Figure 2 illustrates COD removal by both pretreatment systems employed and again demonstrates the effectiveness of optimized DAF treatment. As in subsequent graphs, the data points are not shown to avoid congestion of data.

Fiftieth percentile oil and grease values during Part I of this study were 101, 70, and 16 mg/l for the equalization basin, filter effluent and DAF unit effluent, respectively. The equalization basin 50th percentile TSS level of 78.0 mg/l was reduced to 57.5 mg/l by the filter and to 19.0 mg/l by the DAF unit. A portion of the TSS in the DAF unit effluent was due to biological growth rather than influent solids. It is possible that part of the organics reduction through the DAF unit was the result of biological activity which could also occur in full-scale systems.

2. Part I - Activated Sludge Performance

TOC and COD (filtered) effluent variability plots for pilot-scale 18-hr retention ASU's are compared in Figure 3. These results are from the initial 3-week data run.

Control ASU F produced a better effluent than control ASU A, both operating at equal 0.3 lb TOC/lb MLVSS-day (F/M) loadings. MLVSS levels in ASU A averaged 1,148 mg/l, about twice that of ASU F due to a twofold increase in feed TOC. Considering both TOC and COD removal, ASU B, C, E, and F did not show any significant overall difference in performance. Fiftieth percentile TOC values ranged from 53-58 mg/l while COD values were 97-116 mg/l as shown in Figure 3. Sludge age was not a controlling performance variable as ASU B (50-day SA) and ASU F (about 10-day SA) differed greatly in solids retention time with average MLSS levels of 1,621 mg/l and 816 mg/l, respectively. Chemically assisted pretreatment for removal of colloids and oil had the most significant effect on organics removal. The high-surface-area powdered carbon (designated PC-H) significantly enhanced organic removal in ASU D, with a 50-day SA and a 500-mg/l PC-H operating level. Enhancement was not evident in ASU C containing the conventional-surface-area powdered activated carbon (designated PC-C). Powdered carbon addition increased the average ASU C MLSS level to 1,885 mg/l with ASU D averaging 1,976 mg/l.

Since a marginal enhancement occurred with the addition of PC-H at a 500-mg/l level, the scope of this investigation was expanded to evaluate powdered activated carbon addition at a 1000-mg/l level and only PC-H at approximately 2500 mg/l. This would give a greater overview of the enhancement capabilities of powdered carbon, especially the highly active PC-H. ASU E was taken out of service since it was only succeeding in lysing biological cells as a second stage following ASU B. The reactor was placed in parallel with other units being fed by the DAF unit and redesignated ASU G. The SA was maintained at 50 days and PC-H was built up to a reactor level of about 2500 mg/l for Part II of this study.

3. Part I - Granular Carbon Adsorption

Granular carbon Series A, treating ASU A effluent, exhausted two 130-gram carbon beds during 17 days of a 3.4-gpm/sq ft hydraulic loading in Part I. A 20-mg/l soluble (filtered) TOC and a 44-mg/l soluble COD effluent (50th percentile, Figure 4) was produced with 0.10 and 0.09-g TOC/g carbon accumulative loadings at exhaustion. Carbon Series F, treating ASU F effluent, reduced the 50th percentile effluent soluble TOC and COD to 23 mg/l and 40 mg/l, respectively. Because of the relatively few data points used to establish Figure 4, there is little significance in the difference between carbon series A and F 50th percentile values. A single carbon bed was exhausted to a 0.12-g TOC/g carbon loading. TOC loadings of carbon columns in Series A were comparable to an average of 0.11 g TOC/g carbon reported for the granular carbon during the four previous exhaustions prior to each regeneration.

Granular carbon effluents were of substantially better quality than all biological unit effluents. The 50th percentile soluble TOC and COD reductions in carbon Series A were 44 mg/l and 84 mg/l, respectively, whereas carbon Series F accounted for a 50th percentile 35-mg/l soluble TOC and 65-mg/l soluble COD reduction.

4. Part II - Pretreatment

Pretreatment by filtration and chemically assisted DAF treatment continued as in Part I of this study. Again, using dosages of 40-mg/l filter alum and 20-40 mg/l Dearborn 431, optimized DAF pretreatment reduced the equalization basin TOC and COD by more than 50 percent as shown in Figure 5. Filtration could only remove gross quantities of oil and solids without preliminary chemical coagulation. Although equalization basin, filter, and DAF unit effluent 50th percentile TOC and COD concentrations were approximately equal to those experienced in Part I of this study, there existed a greater degree of variability in Part II. A contributing variability factor was the rainfall dilution of refinery wastewater streams as an average of 0.21 in./day of rain fell during Part II compared with 0.06 in./day during Part I.

5. Part II - Activated Sludge Performance

The effluent quality for Part II, basis filtered TOC and COD, is given in effluent frequency distributions, Figure 6, for the six-week run period. Control ASU A (F/M = 0.3), without optimized pretreatment, continued producing the most inferior effluent and experienced three upsets due to the development of a filamentous bulking sludge. The unit was restarted on each upset occasion with new seed and allowed to acclimate for a few days before effluent data were used for comparison with parallel systems. ASU B, C, and F, as in Part I, produced nearly equivalent effluents in terms of filtered TOC and COD with neither high SA (50 days) nor 1000 mg/l PC-C enhancing biological treatment. PC-H added to ASU D and G at levels of 1000 and 2500 mg/l, respectively, reduced TOC and COD substantially. Compared with high SA control ASU B, 50th percentile TOC was reduced an additional 10 mg/l and 22 mg/l in reactors D and G, respectively. COD 50th percentile reductions below reactor B were 22 mg/l for ASU D (1000 mg/l PC-H) and 39 mg/l for ASU G (2500 mg/l PC-H). The ASU G run time was abbreviated, however, due to the time required for acclimation at the higher PC-H level. As in Part I of this study, it was observed that as powdered carbon levels were suddenly increased in ASU C, D, and G, performance was exceptionally good for a short period of time.

Phenols feed concentrations were higher in Part II of this investigation as 90th percentile values reached 18 mg/l, compared with 8.5 mg/l in Part I. ASU D (see Table 1) and G, containing PC-H, provided the best phenols removal with 50th percentile phenols levels of 0.05 mg/l and 0.04 mg/l, respectively. This was slightly lower than the high SA control ASU B (0.06 mg/l) and low SA control ASU F (0.07 mg/l). Although the lack of optimized pretreatment produced higher 50th percentile phenols levels (0.11 mg/l) in ASU A, even poorer reductions were experienced with ASU C as in Part I. Similar results were obtained in Part I. An occasional high phenols value was measured in the effluents of ASU D and G but not with the consistency or magnitude of ASU C.

Effluent oil and grease values, included in Table 1, illustrate the significance of removing most of the oil and grease before biological treatment. The 18 mg/l 50th percentile oil and grease effluent level of ASU A greatly exceeded the concentration of 5 mg/l, or less, discharged from reactors receiving optimized pretreatment. The addition of PC-H to ASU D and G gave slight oil and grease improvement with SA alone not being an enhancement factor.

Effluent TSS levels were high in ASU A at a 50th percentile level of 86 mg/l. TSS increased to more than 150 mg/l when filamentous sludge bulking occurred. However, ASU's with DAF pretreatment produced a more settleable sludge. The high SA control ASU B had a significantly higher effluent TSS level than the lower SA control ASU F, but the high SA could be maintained. ASU C and D experienced effluent TSS levels less than control ASU B despite higher reactor solids due to powdered carbon. No effluent TSS increase was observed in ASU G due to the higher (2500 mg/l) PC-H level.

Ammonia nitrogen removal in system A was less than the 80 percent achieved in the systems with optimized pretreatment. The organic loading was higher and the sludge age was less than in other systems. The factors controlling the degree of nitrogen removal were not investigated. Nitrification during Part II was not as complete as that obtained in Part I.

Sludge Characteristics and production rates are summarized in Table 2 for all ASU's. As expected, ASU A had the highest measured oxygen uptake averaging 0.16 mg oxygen/l-min due to a higher influent organic concentration. Oxygen consumption averaged 0.10-0.12 mg oxygen/l-min in other ASU mixed liquors, but a relationship of increased oxygen demand and enhanced biological treatment did not exist. The sludge volume index (SVI), a measure of sludge compactability, significantly improved with SA and powdered carbon addition. Sludge settling velocities were exceptionally high with the worst rate (ASU A) being 0.17 ft/min corresponding to a 1830-gpd/sq ft clarifier rise rate. Other mixed liquors settled with zone settling velocities of 0.34-0.39 ft/min. The average MLSS concentration of 745 mg/l in ASU F was too low for zone settling to occur. One of the most surprising results of powdered carbon addition was that less biomass was produced than in control systems. ASU G produced an average of 0.08 lb biomass/lb COD removed compared with control rates of 0.22 for ASU A and 0.19 for ASU F. PC-H was more effective than PC-C at reducing biomass production rates at the same SA. The total sludge production of activated sludge powdered carbon systems was not much higher than controls, due to lower biological sludge production rates.

Powdered carbon inventories and makeup requirements for ASU's are summarized in Table 3 for Parts I and II of this study. PC-C losses were slightly higher than PC-H but still reasonably close to 2 percent per day. Since biological sludge was wasted at a rate of 2 percent per day in high SA reactors, it is a fairly good assumption that powdered carbon lost in effluents was in the same proportion to biological sludge as in the mixed liquor. Thus both biological and powdered carbon SA may be assumed to be equal for simplification of powdered carbon daily makeup requirements. The powdered carbons must be wetted to prevent loss of floating carbon in the clarifier. This was accomplished by boiling the carbon slurry in this study. Vacuum degassing could also be used.

Another observation made during Part II was that activated sludge-powdered carbon systems significantly reduced aeration basin foaming compared with control systems. Foaming in ASU aeration basins was not a problem but did occur occasionally.

6. Part II - Granular Carbon Adsorption

A single granular carbon bed was exhausted from carbon Series A with an accumulative organic loading of 0.15 g TOC/g carbon during Part II. The data include three short runs. The first two carbon beds required backwashing almost daily due to high TSS levels which could not be continuously removed by dual-media filtration. Fiftieth percentile effluent soluble TOC was 30 mg/l (see Figure 7) for a reduction of 38 mg/l from ASU A. ASU A 50th percentile soluble COD was reduced by 84 mg/l to 79 mg/l. Although phenols levels were generally low (50th percentile of 0.04 mg/l) a few very high effluent phenols levels were detected in carbon Series A giving a 90th percentile phenols value of 4.8 mg/l (Table 1). Phenols must have been adsorbed, concentrated, and then eluted in slugs from the carbon beds to achieve such a high level. Effluent oil and grease levels remained low with 50th percentile values less than 3 mg/l.

Carbon Series F exhausted a single carbon bed to an accumulative organic loading of 0.13 g TOC/g carbon while surpassing the performance of carbon Series A. The 50th percentile soluble TOC was significantly lower at 18 mg/l for a 28 mg/l reduction (Figure 7) from ASU F. Fiftieth percentile soluble effluent COD was 64 mg/l for a 44 mg/l reduction. Phenols levels were extremely low at 0.02 mg/l (50th percentile) and no sudden loss of adsorbed phenols was detected during most of the Part II data run (Table 1). Oil and grease effluent levels (50th percentile) were again less than 3 mg/l.

The lower dashed lines in Figure 7 represent the performance of ASU G, the best of the activated sludge-powdered carbon reactors. ASU G produced an effluent superior to carbon Series A and approached the quality of carbon Series F. The powdered carbon enhancement removed about 85 percent of the soluble TOC adsorbed on carbon Series F and about 60 percent of the COD based on 50th percentile effluent values. The 2,500 mg/l PC-H operating level in ASU G significantly reduced effluent color to a level comparable with granular carbon effluent color.

7. Economics

Although unequal in overall performance, a high SA activated sludge-powdered carbon system (ASU G, 72 mg/l COD) approached the level of granular carbon adsorption (carbon Series F, 64 mg/l COD) to within 8 mg/l COD at the 50th percentile point. Both systems would require extensive pretreatment and tertiary suspended solids removal. All other process components being essentially equal, daily carbon usage costs were estimated for theoretical plant flows of 1-5 MM gpd.

The cost of virgin powdered carbon (PC-H or PC-C) was estimated at $0.30/lb and it was assumed that wasted carbon would be thrown away. To calculate the equivalent powdered carbon dosage required for an 18-hr retention ASU it was assumed a 50-day SA would be maintained, giving an average 2 percent powdered carbon makeup. This was the equivalent of a 37.1 mg/l powdered carbon addition rate based on influent flow. A powdered carbon feeder and storage facilities were included in powdered carbon costs using Du Pont economics[16] and applying the 0.6 rule. It was assumed that the powdered carbon feeder could handle a 50 mg/l addition rate.

Regenerated granular carbon adsorption costs were estimated, using Brown and Root, Inc. economics,[29] and converted to 1977 dollars. Daily granular carbon costs were estimated using 17.2 percent of the fixed investment for operating and maintenance cost and 17.7 percent for depreciation. The total daily costs for powdered carbon were estimated using the same percentage allowances.

Daily estimated carbon costs are shown in Figure 8 for theoretical flows of 1-5 MM gpd by scaling up ASU G and carbon Series F carbon requirements. The cost effectiveness of the relatively simple process change of adding powdered activated carbon to the activated sludge process can be clearly seen. Estimated daily cost savings would range from $987/day at 1 MM gpd flow to $2750/day at 5 MM gpd using high-surface-area powdered carbon (PC-H) addition rather than granular carbon adsorption. The incremental cost would be about $14.73 per pound of COD at 1 MM pgd (see Figure 9).

DISCUSSION

1. Increasing Sludge Age (SA)

Contrary to conventional activated sludge design techniques, the increased SA did not result in sludge deflocculation, higher SVI, and high effluent TSS. With the exception of a few days, the high SA control ASU B easily achieved a high SA as a result of good pretreatment as proposed by Grutsch and Mallatt.[10,11] However, no enhanced performance was measured at the high SA nor in the two-stage system with both reactors at a high SA in Part I. Possibly more emphasis should be placed on the benefits of optimized pretreatment than on increased SA as parallel activated sludge systems at about the same SA (F/M = 0.3) were vastly different in performance at contrasting degrees of pretreatment.

Increasing SA gave a reduction in biological solids production as the conventional F/M control ASU F produced 0.19 lb VSS/lb COD removed compared with 0.16 for high SA control ASU B. This sludge production was not quite as significant as it would have been if ASU F had operated at 5-10 days SA where many conventional ASU's operate instead of about 14 days. Any reduction of biological solids production would help lower sludge treatment and disposal costs.

The high effluent 50th percentile ammonia level of ASU A (11.5 mg/l) in Part II was probably the result of upset conditions which resulted from filamentous sludge bulking causing the loss of biomass. The calculated 10-day SA of ASU A was only slightly less than ASU F (14 days) which produced a 50th percentile ammonia level of 2.3 mg/l in Part II. Although increasing SA generally does improve nitrification, no conclusions could be drawn as to its effect in this study. The conventional ASU F had already produced an effluent that was about 90 percent nitrified.

2. Activated Carbon Enhancement Mechanism

A 0.59-g TOC/g carbon loading was calculated in ASU G while operating with a 2500 mg/l PC-H level. This extremely high "apparent" TOC loading, as explained by Flynn,[16] may be the result of continuous adsorption of slowly biodegraded organics which are "biologically regenerated" from the carbon many times over the biological and carbon SA. "Apparent" TOC loadings therefore increase with higher SA, optimizing the use of powdered carbon, until the carbon becomes loaded with completely biorefractory organics. This explanation of an "apparent" loading or enhancement mechanism appears logical; however, oxygen uptake and biological sludge production data presented here negate biological regeneration in this study. ASU G not only had comparable oxygen uptake measurements with control ASU B, but it produced about 50 percent less biological solids. This implies that the actual enhancement may have been predominantly due to adsorption on the high PC-H surface area. Considering that PC-H had approximately five times the surface area of conventional powdered carbons, such as PC-C, the expression of the TOC loading as 0.12 g TOC/500 sq m of surface area would be more reasonable.

DeJohn[19,30] explains that granular carbon columns are sometimes undersized because the designer uses virgin carbon and assumes that regenerated carbon will have the same activity. The thermal regeneration process will enlarge some carbon pores reducing the surface area and decreasing the adsorption of small molecules which are not so strongly adsorbed on larger pores. Assuming that many small molecules require small powdered carbon pores for moderately strong adsorption, PC-H may have been more effective than PC-C because of pore size distribution, provided that the normally biorefractory refinery organics were small molecules.

The mechanism of powdered carbon enhancement of the activaged sludge process was not defined in this study and needs further investigation in Phase II. Target SA's of the activated sludge-powdered carbon systems were 50 days. Ideally, systems should be operated for periods of several SA's to insure that equilibrium conditions have been reached and that the low (2 percent) daily powdered carbon makeup rate will continue to give consistent results.

The selection of the best powdered carbon for a particular activated sludge enhancement is not a simple task since powdered carbons vary in their adsorptivity. Carbon isotherms performed on a refinery wastewater would exhibit a wide variability and require a statistical analysis to select the best powdered carbon. Isotherms would have to be performed on the activated sludge effluent (as in Phase II of this study) to determine enhancement strictly due to adsorption.

The powdered activated carbon (PC-H) utilized with very good enhancement results is not, as of yet, commercially available. Because of the relatively high cost of granular carbon adsorption, other powdered carbons at similar and higher operating levels would probably offer a significant improvement in activated sludge performance and remain more cost effective than granular carbon.

3. Granular Carbon Adsorption

Granular carbon adsorption data indicate that the quality of end-of-pipe refinery wastewater treatment depends on optimization of each treatment step from primary to tertiary treatment. The use of equilibrium or regenerated granular carbon in pilot studies will provide a more realistic data base, recognizing that economics would favor regeneration for many potential users.

The classical approach[31,32,33,34] for handling carbon adsorption data to establish breakthrough curves was virtually useless in this study because it assumes the carbon column influent has a single adsorbate. In the calculation of accumulated TOC loadings at apparent breakthrough of carbon columns there were several instances where organics were eluted in slugs from carbons in both series. At times, phenols were two orders of magnitude higher than normal. This phenomenon is a very real problem and must be considered when establishing stringent effluent discharge guidelines for industry. Even the best available technology, disregarding economics, has its limitations.

SUMMARY

The EPA 1983 guidelines for the petroleum refining industry have assumed that 1977-type technology must be upgraded by the addition of costly systems, such as granular activated carbon adsorption. The results of this API study indicate that, should the EPA adhere to the granular carbon technology originally proposed, it may be possible to achieve this level of treatment technology by the much more cost-effective method of adding powdered activated carbon to the 1977 activated sludge system.

Process modifications including optimized pretreatment and the addition of a high-surface-area powdered activated carbon can be used to produce an effluent which is comparable in quality to that obtained by granular carbon adsorption. Increasing activated sludge age from the conventional mode of operation (about 10 days) to about 50 days did not give a significant system improvement; however, in conjunction with powdered carbon addition, high sludge age allowed higher equilibrium reactor concentrations (2500 mg/l) at low (2 percent) carbon makeup rates. This benefit has been demonstrated with the high-surface-area carbon and it is possible that it can also be obtained with increased levels of conventional powdered carbon. The cost-effectiveness of any powdered carbon will depend on the wastewater characteristics and powdered carbon adsorptivity, which was greater for the high-surface-area carbon (2462 sq m/g) than for the conventional-surface-area carbon (550 sq m/g) investigated here. Even granular carbon adsorption was found to have limitations as slugs of phenols were eluted, on occasion, into the effluent.

ACKNOWLEDGEMENTS

This study was funded in part by the American Petroleum Institute, Divison of Refining, CREC Liquid Waste Subcommittee.

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BIOGRAPHY

Leonard W. Crame

Leonard W. Crame is a Senior Chemical Engineer in the Air and Water Conservation Section of Texaco's Prot Arthur, Texas, Research Laboratories. He has a B.S. degree in Engineering Technology (Chemical) and an M.S. in Thermal and Environmental Engineering from Southern Illinois University at Carbondale. Len has been involved in several refinery wastewater treatment pilot studies and conceptual designs since joining Texaco in 1973. He is a member of the Texas Water Pollution Control Association and has recently authored several papers on wastewater treatment.

DISCUSSION

E. A. Buckley, Lion Oil Co.: What were the levels of alum and polyelectrolyte used in the DAF pretreatment to the system?

Len Crame: In the dissolved air flotation unit we were using, we found by the use of the zeta meter and jar tests that it required 40 milligrams per liter of filter alum, 20 milligrams to 40 milligrams per liter of catonic polymer Dearborn 431. It was not the intent of this study to try to zero in on the best and most economical chemical dosage but mainly to get the soluble feed for the bio units. We found from experience that wide fluctuations in the feed characteristics did not affect these two chemical doses.

Ed Sebesta, Brown & Root: In the slide (Figure 2) comparing effluent and COD concentrations from the various pretreatment systems, were the samples filtered or unfiltered?

Len Crame: They were filtered COD's for our bio effluents and carbon effluents. In Figure 2, I did not identify them, but it is total COD. It does include suspended solids because we were looking for the contribution of solids in this case.

I also would like to make the comment that I do pretty much agree with everyone else's presentations as far as what work has been done with carbon on the enhancement mechanism and we will continue to look at this throughout the second phase of our pilot study. I think that you have to be very careful in using powdered activated carbon. In a short term study I agree with the other gentlemen (Amoco)(DuPont), that when you first put in activated carbon you have to allow time for this matrix to form, which we did. And you don't get the same settling effect as when you initially add carbon. When you allow the system to come to an equilibrium and the bio-mass starts adhering to the powdered carbon, it does greatly improve the sludge settling characteristics, but it takes a little time. I believe that when you initially add powdered carbon your results are going to be very good because you're going to get a tremendous amount of adsorption. We followed this and have seen it. I'm very hesitant about including data right after you start running an enhanced bio-system. You will see a sharp decrease in the effluent organic levels. You have got to wait until an equilibrium is reached.

J. Dewell, Phillips Petroleum Co.: In your cost comparison between enhanced activated sludge and the granular carbon, I wasn't sure if the enhanced activated sludge assumed that the conventional activated sludge was already in place or not. Would these comparisons still be valid on a grass-roots treating system?

Len Crame: We were assuming that activated sludge was already in place and actually we were only comparing the cost of carbon contactors and regeneration equipment against the additional equipment you have to put in to add powdered carbon. We were not including filters. We would believe the filter would have to be a part of both treatment systems and would have no effect on this comparison.

J. Dewell: Do you have any feel for what would be most cost effective on a grass-roots basis, assuming no treatment system at all exists?

Len Crame: I think it is a safe argument that activated sludge is probably the best system for driving the effluent organic levels down for 1977 and 1983 but not necessarily the most cost effective. At this time I do not see any other system that perhaps can be enhanced cost effectively with powdered carbon for 1983.

J. Dewell: I was referring to a situation where one does not have activated sludge at this time and is meeting 1977 standards so one is going to come to 1983 without any activated sludge.

Len Crame: I think this must be determined on an individual basis. As you know when you calculate out guidelines for '77 or '83 you will find that in some cases you are stuck with very tight guidelines for a certain parameter and I don't think it is appropriate to say which type of treatment would be best. We would definitely not put in any powdered-carbon enhanced system until we piloted it and you would be taking a risk if you did. All treatment systems are unique, including activated sludge systems and enhanced biological systems. We think that powdered carbon addition has a lot of merit, but still you should determine it on a case-by-case basis.

F. L. Robertaccio, DuPont: I think that the easiest way to look at it is that the activated sludge system in this case is common to both the powdered-carbon addition and the granular-carbon addition system so the difference in cost here would have added to it the cost of the activated sludge system if you were starting out with a brand new plant. You can use that as a first estimate, but what we have found at the plant I talked about yesterday is that with a grass-roots plant you have additional savings that you can accrue to take full benefit of the system. We talked about having smaller secondary clarifiers, higher upflow rates through the clarifiers, smaller dewatering equipment; and having no secondary solids disposal if you go through regeneration. So our experiences have been that with the grass-roots system you can put in powdered carbon systems with regeneration for the same capital costs and essentially the same operating costs as a conventional secondary wastewater treatment system. If you want further reference on this there was a paper I referred to yesterday that had details of those cost estimates.

J. E. Rucker, API: Please comment on why your COD values were greater than those we looked at earlier this morning from the Argonne work?

Len Crame: The refinery where we were located is a very complex refinery and I am quite sure that the refractory COD that remains is going to differ from plant to plant. We did try to exclude everything from the chemical plant, but I am not surprised really that we have a different refractory COD level and I don't think you can compare the refractory COD's out of these carbon systems from plant to plant and find a great consistency as far as concentration goes.

Jeffrey Chen, Dravo: What would you propose to use to treat the sludge generated from the pretreatment unit? Will the cost associated with the treatment be cost effective when compared to the improvement of the following bio system?

Len Crame: We were assuming that for our best case here that when we were comparing granular carbon with powdered carbon you would have a primary sludge treatment and disposal problem in both cases so that it really doesn't affect our economics here. Sludge disposal is another problem and again it does depend upon the availability of land and other considerations and it is just something totally different; but actually we're comparing the two systems here and assuming that primary sludge is going to be a problem in both cases. You would have to do a cost effectiveness study on the pretreatment and sludge disposal cost vs the benefit obtained from it. But from an operational standpoint, once you get the colloids and oil out it is much easier to operate the activated sludge process, since the oil and solids interfere with flocculation and sludge settling.

Tom McConomy, Calgon Corp.: During the period you were operating the granular carbon columns, was the carbon changed or was the same carbon used during the entire test?

Len Crame: As you will see in the paper we had four carbon columns and we would measure TOC at intermediate points and whenever we found a breakthrough on the first carbon column, we would shift the carbon columns and put a fresh regenerated column on the tail-end of the system. This is why we are confident that the final column effluent is representative of what carbon adsorption can do with the regenerated carbon. We did try to determine how much we had in those columns and we were running about 0.12 to 0.15 pounds TOC per pound of carbon, which I think is fairly typical. But because of the activated sludge enhancement you get with powdered carbon, where I won't necessarily say "biological regeneration" occurs, you are effectively regenerating it somehow by desoprtion, or whatever, within the process and that is what makes it economical.

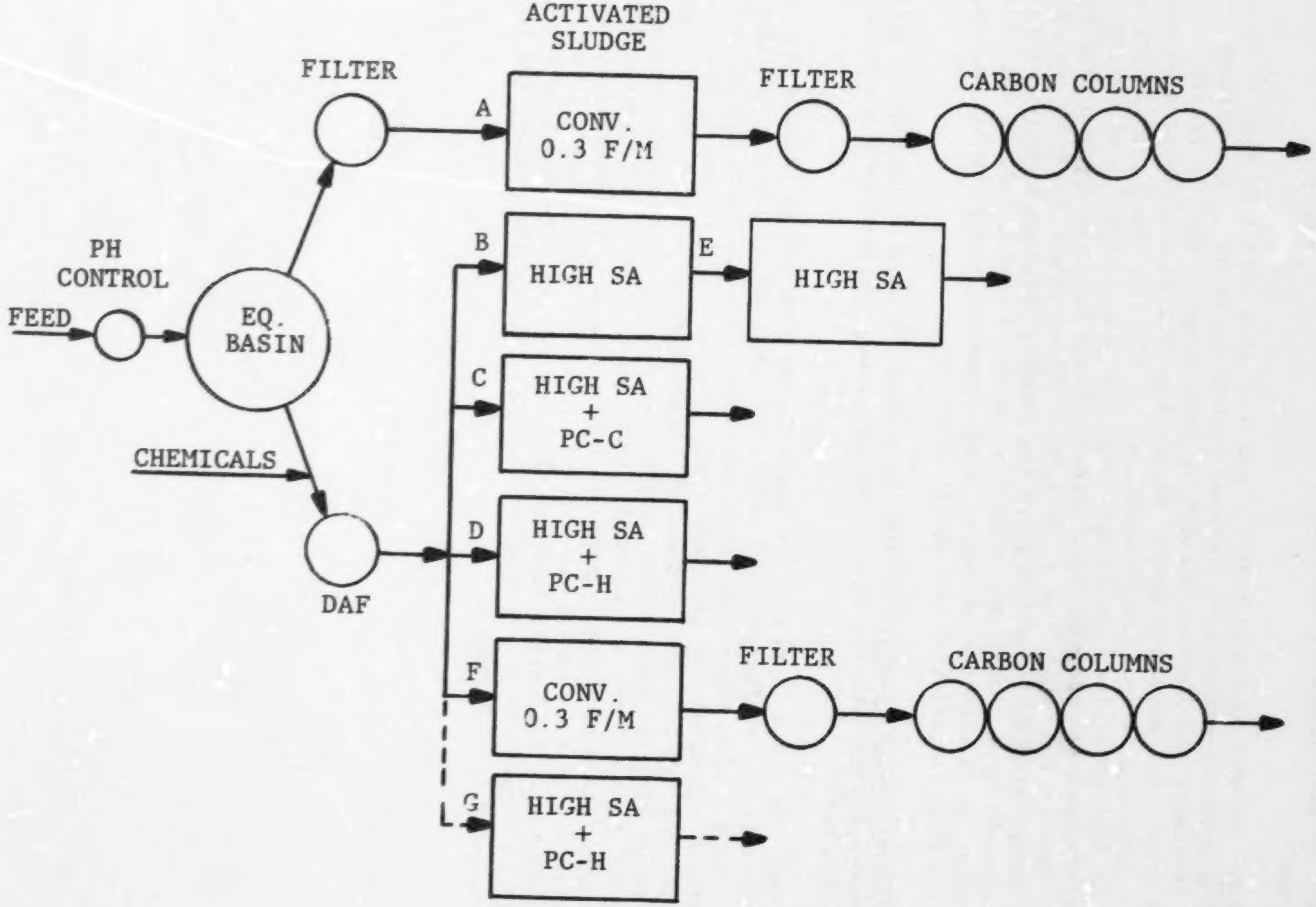


FIGURE 1 - TREATMENT SCHEMES

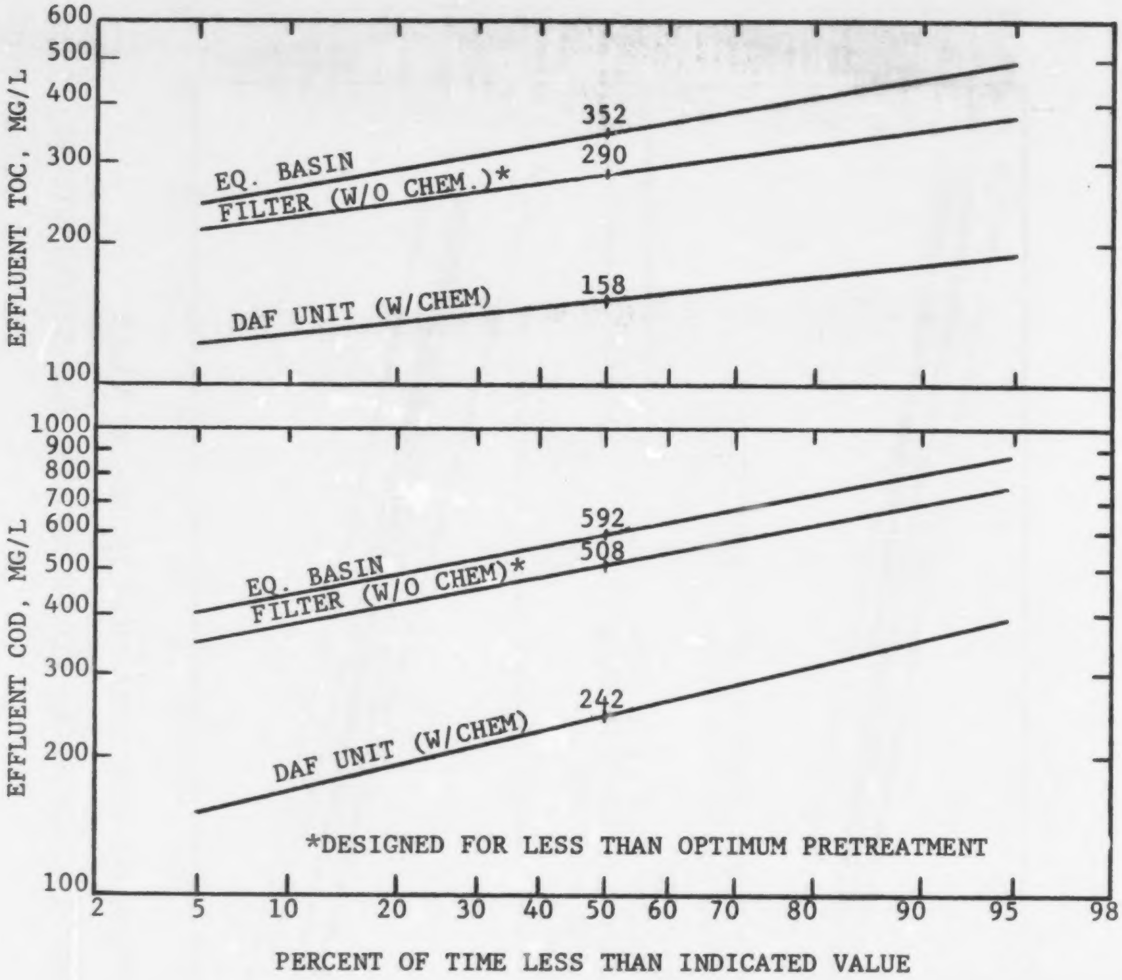
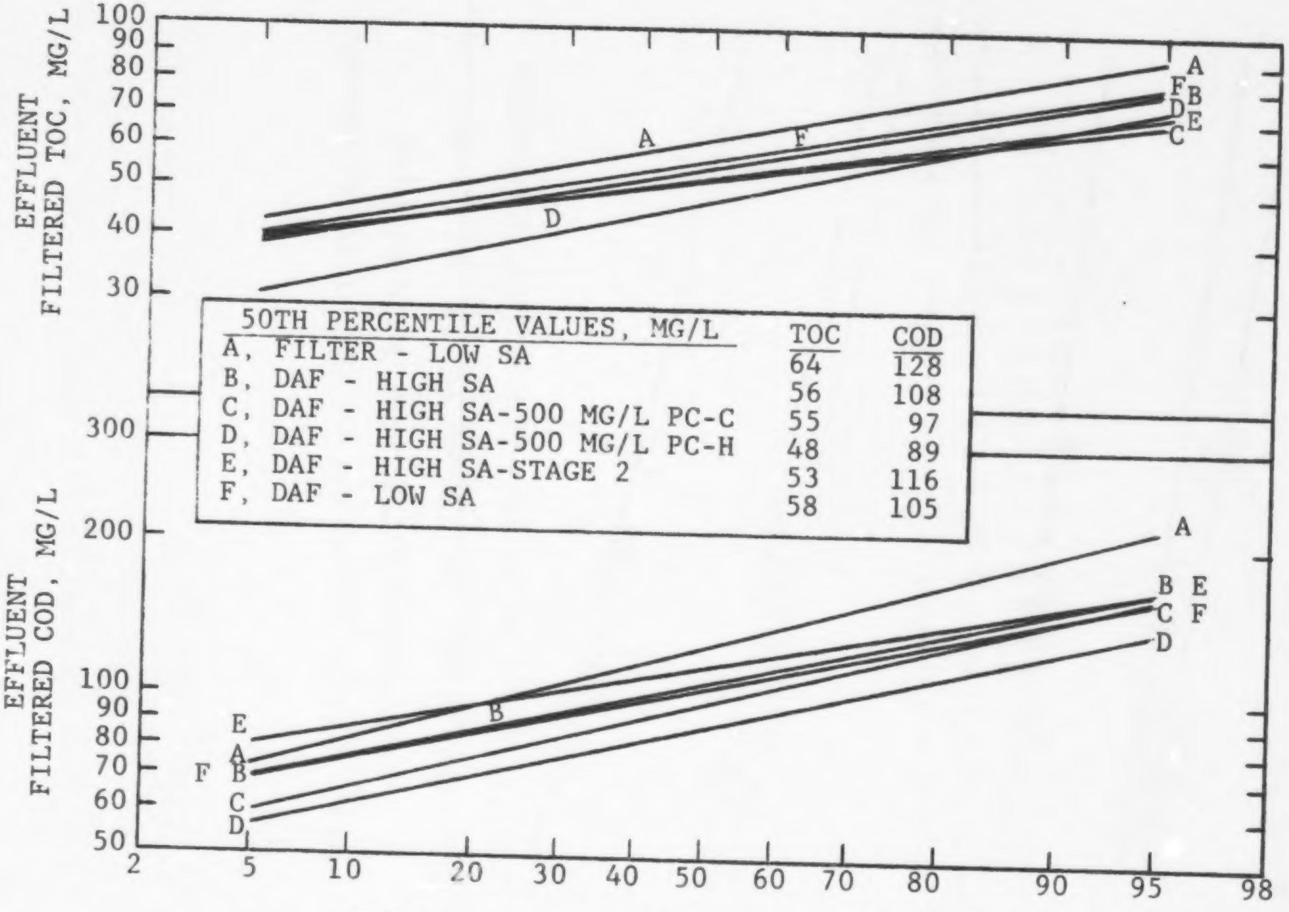


FIGURE 2 - PART I - TOC AND COD REMOVAL BY PRETREATMENT



50TH PERCENTILE VALUES, MG/L	TOC	COD
A, FILTER - LOW SA	64	128
B, DAF - HIGH SA	56	108
C, DAF - HIGH SA-500 MG/L PC-C	55	97
D, DAF - HIGH SA-500 MG/L PC-H	48	89
E, DAF - HIGH SA-STAGE 2	53	116
F, DAF - LOW SA	58	105

FIGURE 3 - PART I - ACTIVATED SLUDGE TOC AND COD DISTRIBUTIONS

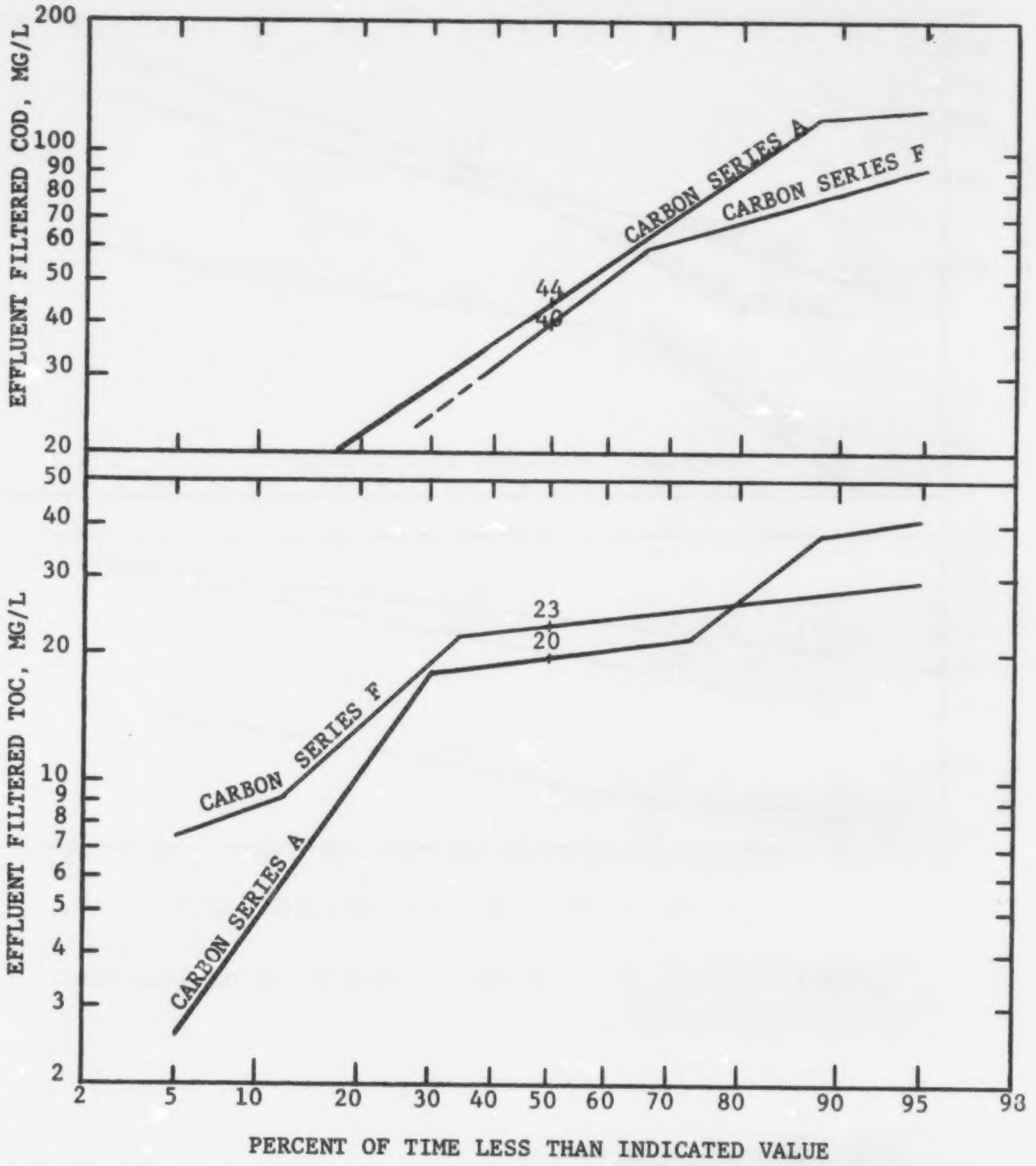


FIGURE 4 - PART I - GRANULAR CARBON COLUMN TOC AND COD DISTRIBUTIONS

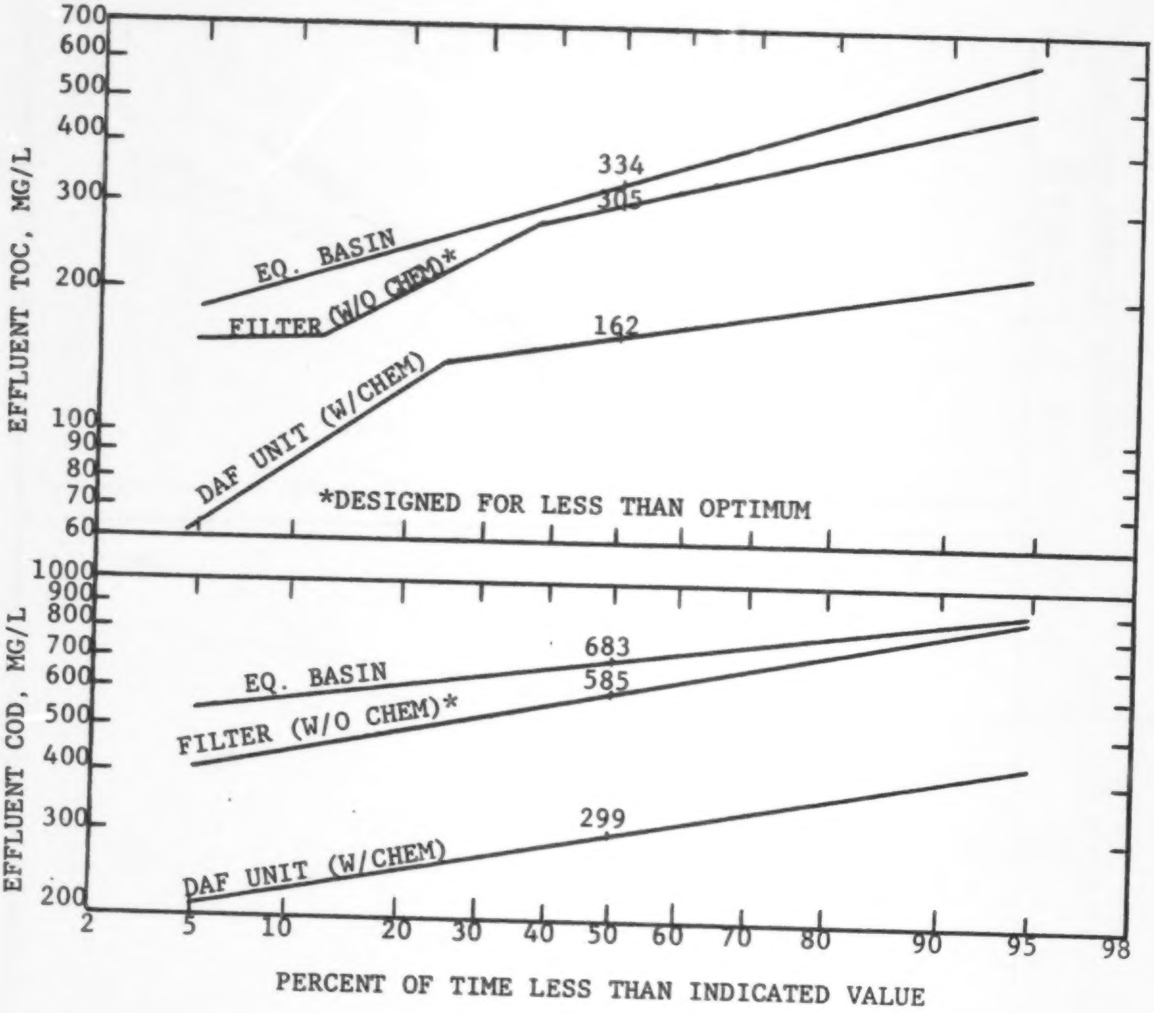
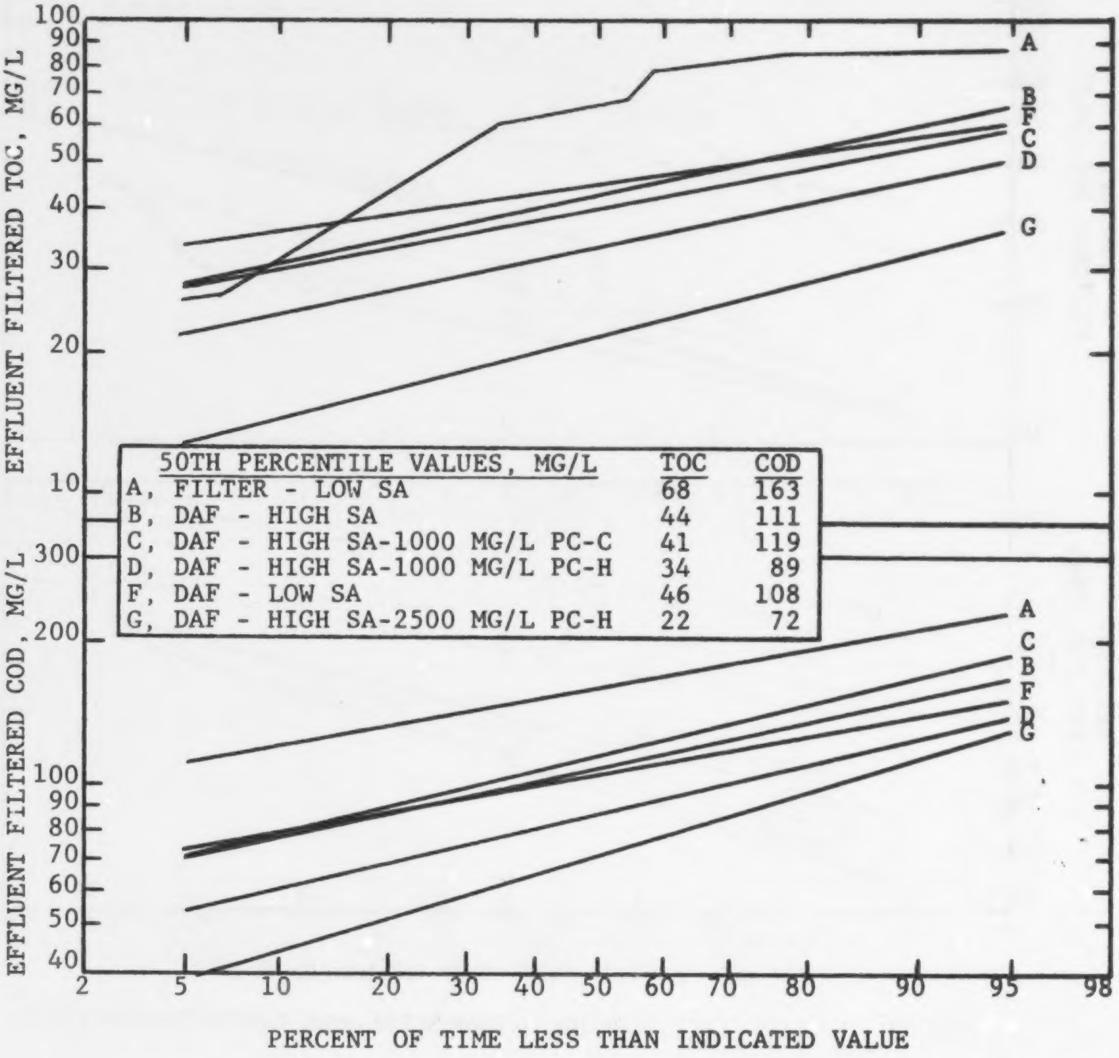
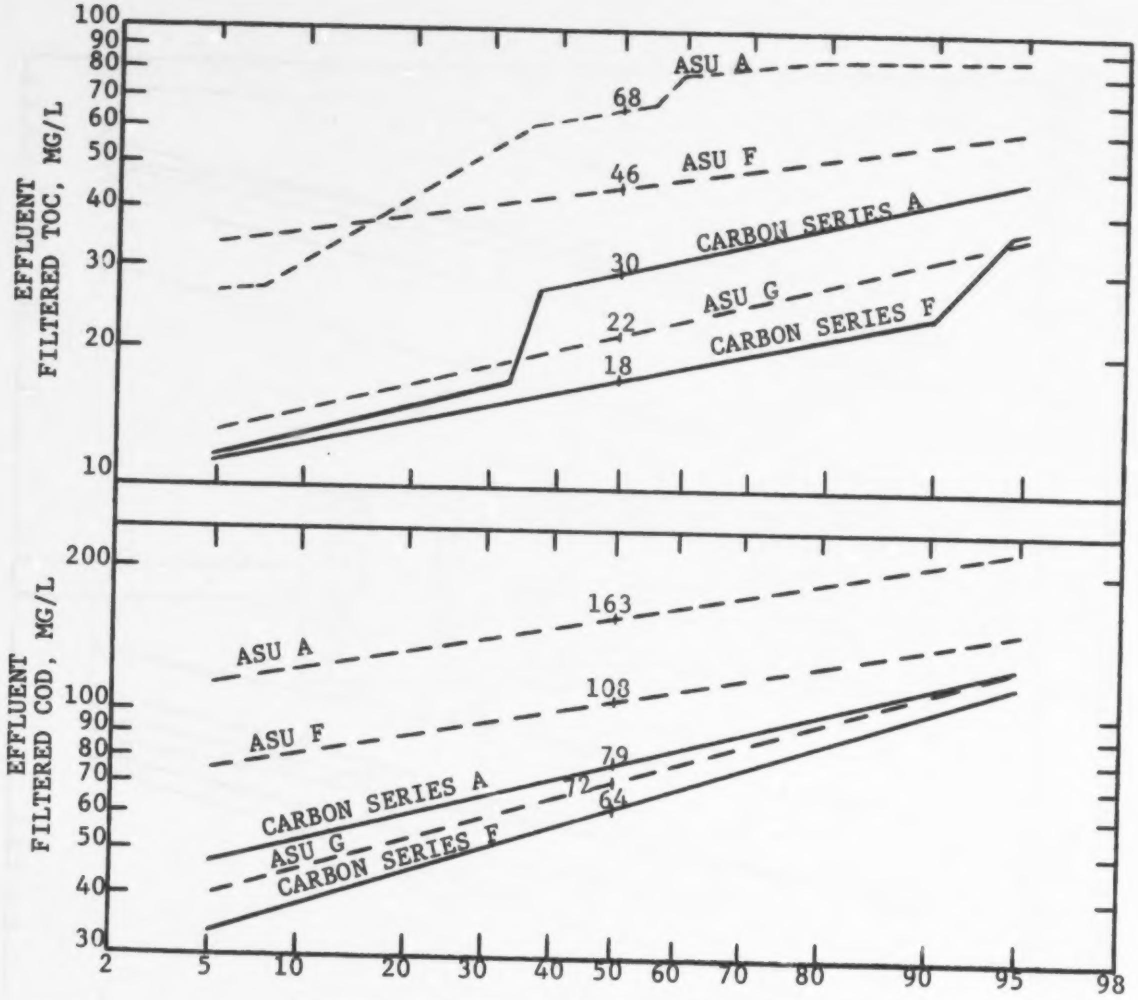


FIGURE 5 - PART II - TOC AND COD REMOVAL BY PRETREATMENT



50TH PERCENTILE VALUES, MG/L	TOC	COD
A, FILTER - LOW SA	68	163
B, DAF - HIGH SA	44	111
C, DAF - HIGH SA-1000 MG/L PC-C	41	119
D, DAF - HIGH SA-1000 MG/L PC-H	34	89
F, DAF - LOW SA	46	108
G, DAF - HIGH SA-2500 MG/L PC-H	22	72

FIGURE 6 - PART II - ACTIVATED SLUDGE TOC AND COD DISTRIBUTIONS



PERCENT OF TIME LESS THAN INDICATED VALUE

FIGURE 7 - PART II - GRANULAR CARBON TOC AND COD DISTRIBUTIONS

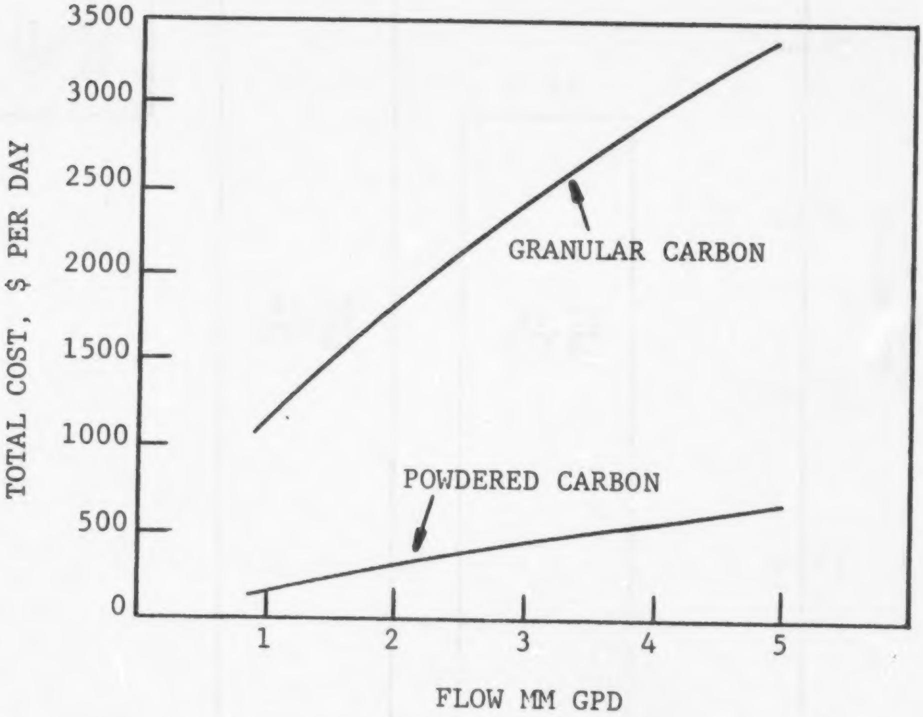


FIGURE 8 - COMPARISON OF ESTIMATED CARBON COSTS

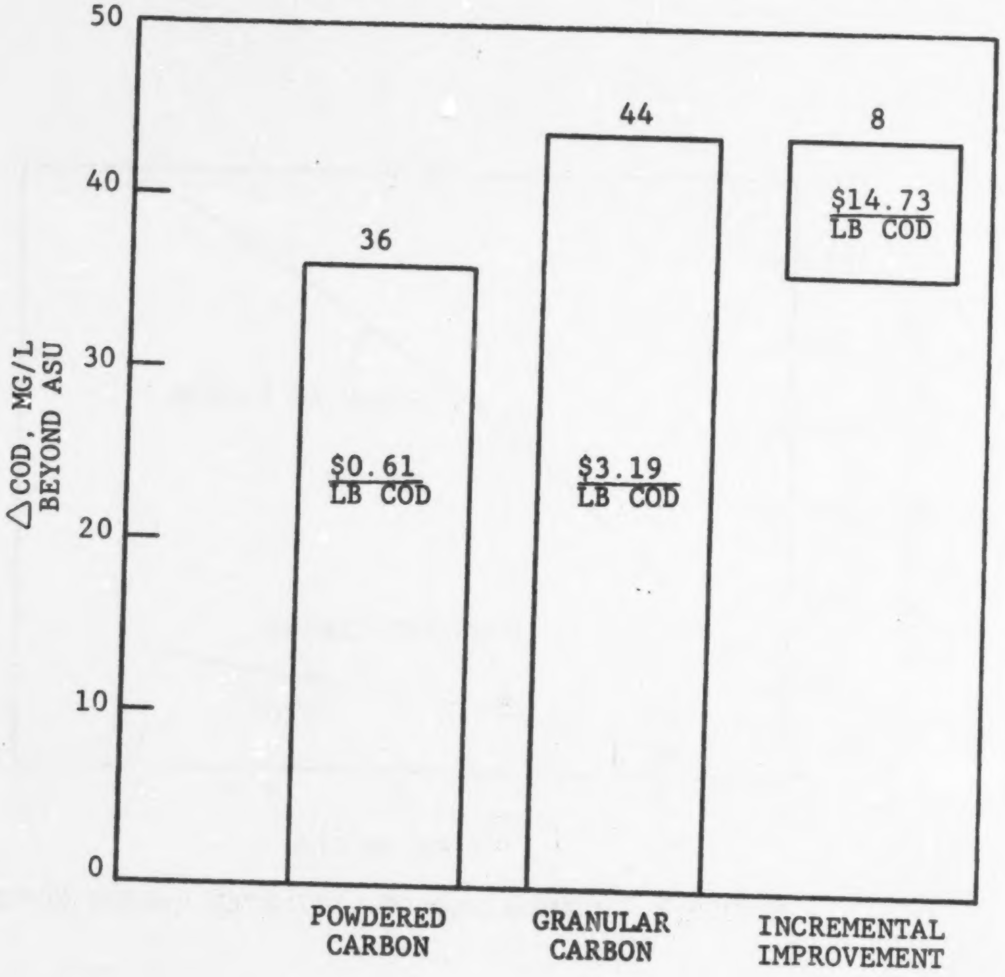


FIGURE 9 - ESTIMATED EFFECTIVE CARBON COST AT 1 MM GPD

TABLE 1- PART II - EFFLUENT SUMMARY

(ALL VALUES MG/L)

EFFLUENT SAMPLE	PHENOLS PERCENTILE		OIL & GREASE PERCENTILE		TSS PERCENTILE		AMMONIA PERCENTILE	
	50TH	90TH	50TH	90TH	50TH	90TH	50TH	90TH
EQ BASIN	7.3	18.0	108	191	64.0	119	20.9	27.2
FILTER	—	—	69	130	34.0	74.0	—	—
DAF UNIT	--	--	14	19	13.0	21.0	—	--
ASU A	0.11	0.16	18	38	86.0	149	11.5	20.0
ASU B	0.06	0.14	5	7	27.5	41.0	3.9	9.2
ASU C	0.15	0.38	3	9	23.0	77.0	3.3	5.4
ASU D	0.05	0.20	< 3	5	18.0	57.0	3.1	4.8
ASU G	0.04	0.13	< 3	3	22.0	44.0	3.1	4.4
ASU F	0.07	0.17	4	7	8.4	28.0	2.3	5.4
CARBON COL. (SERIES A)	0.04	4.8	< 3	6	--	--	--	--
CARBON COL. (SERIES F)	0.02	0.08	<3	4	--	--	—	—

TABLE 2 - PART II - SLUDGE DATA

AVERAGE VALUE	ACTIVATED SLUDGE UNIT A	B	C	D	F	G
NOMINAL LOADING	F/M = 0.3	50-DAY SA	50-DAY SA	50-DAY SA	F/M = 0.3	50-DAY SA
ACTUAL LOADING	F/M = 0.3	39-DAY SA	42-DAY SA	44-DAY SA	F/M = 0.3	56-DAY SA
MLSS, MG/L	1,487	1,892	2,728	2,720	745	4,096
MLVSS, MG/L	1,302	1,562	2,269	2,416	689	3,898
PC, MG/L	0	0	1,000[a]	1,000[b]	0	2,500[b]
% VSS	88	83	83	89	92	95
OXYGEN UPTAKE, LB O_2/LB COD REM	0.40	0.68	0.71	0.49	0.61	0.47
MG/L-MIN	0.16	0.12	0.12	0.11	0.11	0.10
SVI, ML/G	95	64	41	43	91	30
SETTLING VELOCITY, FT/MIN	0.17	0.34	0.38	0.38	N/A[c]	0.39
BIOMASS PRODUCTION RATE[d]	0.22	0.16	0.12	0.11	0.19	0.08
TOTAL PRODUCTION RATE[e]	0.25	0.19	0.17	0.14	0.21	0.09

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[a] CONVENTIONAL-SURFACE-AREA.
[b] HIGH-SURFACE-AREA.
[c] DISCRETE SETTLING
[d] LB VSS/LB COD REMOVED.
[e] LB TSS/LB COD REMOVED (INCLUDES CARBON)

TABLE 3 - POWDERED CARBON (PC) REQUIREMENTS

ASU-PART	PC LEVEL (MG/L)	PC TYPE	PC INVENTORY (G)	AVG PC LOSS (G/DAY)	PC MAKEUP (%)
C-I	500	PC-C	28.4	0.68	2.4
D-I	500	PC-H	28.4	0.56	2.0
C-II	1,000	PC-C	56.7	1.50	2.6
D-II	1,000	PC-H	56.7	1.12	2.0
G-II	2,500	PC-H	141.9	2.21	1.6

SESSION IX

COSTS/BENEFITS

Chairman

Thomas L. Hurst

Corporate Director of Safety and Environmental Services
Kerr-McGee Corporation, Oklahoma City, Oklahoma

Speakers

W. Wesley Eckenfelder, Jr.
"Overview of Costs/Benefits"

Lial F. Tischler
"Treatment Cost-Effectiveness as a Function of Effluent Quality"

Carl E. Adams, Jr. and John H. Koon
"The Economics of Managing Refinery Sludges"

Melville Gray
"Compliance Monitoring Costs for the Priority Pollutants"

Robert F. Babcock, Leo J. Duffy and Gilbert G. Jones
"Analytical Costs in the Problem Pollutants"

BIOGRAPHY Thomas L. Hurst

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"OVERVIEW OF COSTS/BENEFITS"

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INTRODUCTION

It is difficult to interpret cost/benefits in the classic sense when considering present water pollution control limitations for industrial effluents. Two cases will be considered, the first involving a water quality limiting discharge, and the second related to present effluent guideline limitations.

A water quality limiting discharge will usually involve effluent requirements more stringent than that imposed by effluent guidelines and in many cases require wastewater treatment beyond conventional secondary treatment processes. This discussion will relate to parameters pertinent to the oxygen balance in the receiving water and the cost effectiveness of wastewater treatment relative to this impact.

WATER QUALITY

Several factors should be considered in the water quality limiting case. A mixed wastewater may contain many organics of varying biodegradability. The overall rate will be the sum of the individual rates. For example a recent study involving treatment in the activated sludge process using a mixture of glucose, phenol and sulfonilic acid showed individual removal rates of 0.072 mg/mg/day, 0.049 mg/mg/day and 0.015 mg/mg/day respectively with an overall removal rate of 0.130 mg/mg/day. The removal rate coefficient K can be computed from Equation (1)

$$\frac{S_o - S_e}{X_v t} = K \frac{S_e}{S_o} \tag{1}$$

The biodegradation rate coefficient, K, as defined by Equation (1) reflects the overall rate for the wastewater in question. Removal of the more readily degradable organics through a treatment facility, i.e. the glucose and the phenol in the above example, will cause a reduction in the deoxygenation rate coefficient (K) of the residual organics discharged to the receiving stream. For example, a raw wastewater might exhibit a BOD rate coefficient of 0.25/day, while after treatment and removal of the readily degradable organics, the resulting BOD rate coefficient might be 0.08/day. Hypothetically, discharging the same pounds of BOD will cause less of an oxygen deficit if the deoxygenation rate is low as opposed to a high K rate, as shown in Figure 1. This illustrates the fallacy of only considering the lbs. of BOD discharged without regard to the resulting deoxygenate rates in the receiving stream. Therefore, relative to the impact on the receiving stream, both the quantity of BOD as well as the biodegradation rate of the residual BOD should be considered. The effect of biodegradability on activated sludge plant costs are shown in Figure 2. It becomes apparent that for cost effective design, higher concentrations of effluent soluble BOD can be discharged for wastewaters of low biodegradability without as significant an effect on the oxygen balance in the receiving stream.

There is an increasing emphasis today on nitrification in a wastewater treatment facility, particularly as it relates to the oxygen balance in the receiving water. Removal of carbonaceous organics may move the nitrification oxidation upstream closer to the wastewater discharge resulting in greater depletions of oxygen. This phenomena is accentuated when the wastewater treatment plant is nitrifying and thereby discharging increased numbers of nitrifying organics to the stream. Temperature has a major effect on the nitrification process, both in the treatment plant and the receiving stream. A cost effective wastewater treatment plant might be designed to produce nitrification during the summer months when oxygen depletion into the receiving stream would be greatest. Nitrification would not be significant during the winter months when the nitrification rate in the stream and the resulting numbers of nitrifyers from the plant would be minimal. The effect of temperature on nitrification design and resulting costs is shown in Table 1.

TABLE 1 "EFFECT OF TEMPERATURE ON NITRIFICATION DESIGN AND COSTS"

RAW WASTE LOAD	10 mg/1 150 mg/1 BOD 20 mg/1 NH_3-N	
EFFLUENT QUALITY	15 mg/1 BOD 2 mg/1 NH_3-N	
TEMPERATURE, ^{o}C	10	25
SLUDGE AGE, DAYS	14	5
AERATION BASIN VOLUME, MIL. GAL.	2.0	1.0
AERATION, HP	200	170
CONSTRUCTION COST	$696,000	$481,000

Significant capital and operating costs for construction and power are required to achieve nitrification under cold conditions. Another factor which needs to be considered in the oxygen balance in the receiving stream is the fact that many substances that depress the reaeration coefficient, such as surface active agents present in raw wastewaters, are removed in wastewater treatment. The net effect is to increase the reaeration coefficient in the receiving water with increasing degrees of wastewater treatment. This has the net effect of permitting higher organic loads without further oxygen depletion. Because of the nature of the biodegradation process, both in the wastewater treatment plant and the receiving stream, cost effective design and operation should lead to a two-tiered standard in those parts of the country where cold weather temperatures effect the biological oxidation process, both in the treatment facility and in the receiving water.

EFFLUENT GUIDELINES

The second case considers those plantssubject to effluent guideline limitations. It should be recognized that most industrial plants are or will be coming into compliance with Best Practicable Control Technology (BPT) regulations effective July 1, 1977. This would imply that most industrial plants discharging organic wastewaters will have installed biological wastewater treatment, and that any consideration of additional reduction in pollutional loads should consider the existence of a biological wastewater treatment facility at that time. The original effluent limitations relating to Best Available Technology Economically Achievable (BATEA) generally considered some in-plant reductions in wastewater volume and principally add-on end-of-pipe treatment units such as filtration and carbon adsorption. Cases that have been evaluated by the writers would indicate that other approaches to effluent quality improvement may be considerably more cost effective than indiscriminant add-on treatment facilities. These approaches are:

1) In-plant changes to eliminate or reduce pollutional loads.

2) Installation of treatment systems for process modification at specific discharge sources to eliminate, reduce or modify the wastewater characteristics to render them more compatible with existing wastewater treatment facilities.

3) Add-on tertiary treatment units to the existing wastewater treatment facility.

A detailed study was conducted for the Effluent Standards and Water Quality Information Advisory Committee (EPA) in order to define the cost effectiveness of pollution reduction by in-plant changes with existing treatment facilities as compared to additional end-of-pipe wastewater treatment as defined by the then BATEA criteria. This study considered an activated sludge plant in place at the time improved effluent quality was to be considered. The alternatives considered are coagulation, filtration, carbon adsorption and in-plant changes to reduce wastewater flow and strength. The in-plant changes include equipment revision and additions, unit shut downs, scrubber replacement, segregation, collection and incineration, raw material substitutions, reprocessing and miscellaneous small projects. Table 2 summarizes the results of this study. Cost relationships for COD removal for the various options are shown in Figure 3. It is apparent that little benefit in effluent quality is gained by adding carbon adsorption to the activated sludge plant effluent over in-plant changes with biological and chemical treatment. As can be seen, additional end-of-pipe treatment, including filtration and carbon adsorption, resulted in an increased removal of 23,930 pounds of COD per day at an annual additional cost of $4.1 million dollars per year. In contrast, in-plant changes with minimal additional treatment, i.e., chemical coagulation and filtration, resulted in a COD reduction of 19,260 pounds per day at a cost of $1.3 million dollars per year. It is readily apparent from Figure 3 that a cost effective analysis would mitigate against the application of carbon adsorption for the minimal improvement in effluent quality achieved.

In most cases, effluent treatment facilities have been designed to treat total wastewater discharges to levels consistent with effluent guidelines limitations established by EPA for specific industrial categories and subcategories. In many cases, removal of particular constituents which are inhibitory to the biological treatment process or possess a very low degradation rate, by treatment of these constituents at their source can result in a marked improvement in performance and an increase in capacity of existing biological wastewater treatment facilities. Table 3 illustrates a case in which one wastewater stream markedly reduced the overall biodegradation rate in the biological wastewater treatment facility.

TABLE 3 "REACTION RATE COEFFICIENTS WITH AND WITHOUT CARBON PRETREATMENT OF A PESTICIDE WASTEWATER"

	Non-Carbon Treated	Carbon Treated
T °C	K 1/day	K 1/day
28°C	2.25	23.1
8°C	0.81	6.5

Removal of this constituent by separate carbon adsorption treatment rendered the total wastewater stream considerably more degradable. This would substantially reduce the effluent pollutant levels from the biological treatment facility or permit higher organic loadings through the facility with resultant reductions in effluent discharges. An evaluation of both the biodegradability and the effect of wastewater constituents on biodegradation on specific sources within the industrial facility should in many cases lead to marked improvement in both wastewater treatment plant operation and effluent variability. This is particularly true where new products are to be introduced into the plant which may affect the overall biodegradation characteristics.

A few years ago post-tertiary treatment from the petroleum and chemicals industries generally considered filtration followed by granular carbon adsorption columns. Recent developments in the field show promise for other processes and process modifications which are considerably more cost effective for further pollutant reduction. These include the application of polymers or coagulants prior to the final clarifier for improved suspended solids reduction. This approach involves minimal capital expenditures. The application of powdered activated carbon in conjunction with the biological treatment process has shown considerable promise in recent plant and pilot plant studies. In fact, several papers at this seminar have reported on the results of such studies. Modification to post filtration systems using modified media, such as compacted clay or coal, to encourage and enhance biological action has shown the capability of reducing effluent soluble BOD levels to less than 5 mg/l and suspended solids to less than 10 mg/l. In this case post filtration serves the dual purpose of removal of suspended solids and further biological oxidation, since oxygen is limiting BOD reductions in the order of 10-20 mg/l are feasible. In some cases, depending on oxygen limitation, nitrification might also be achieved in this process. Most of the data available to the writers at this time involves application of this process to domestic wastewater. Further experimental studies would be required to indicate the feasibility of applying such processes to tertiary treatment of industrial wastewaters.

BIOGRAPHY

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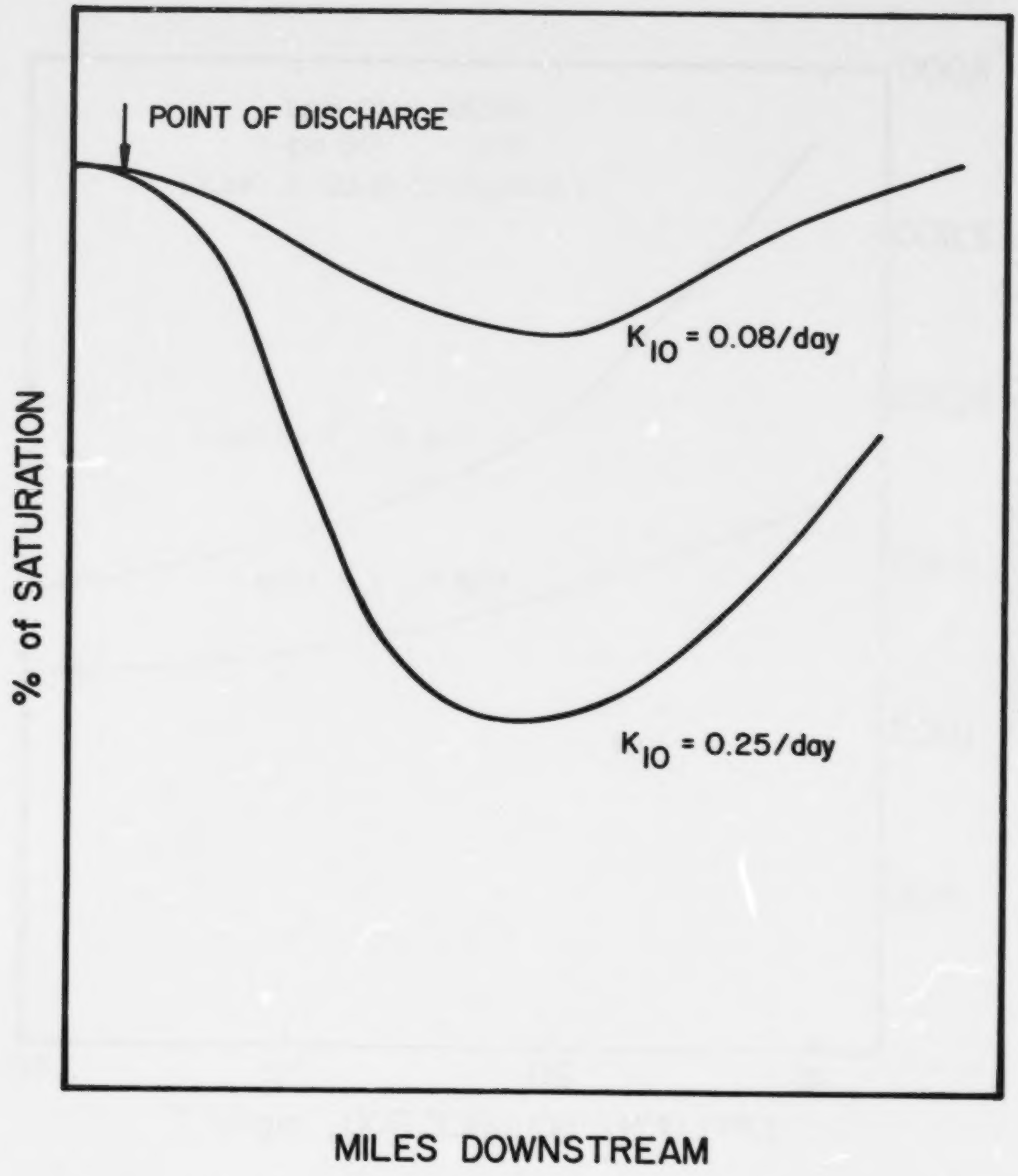

FIG. 1. EFFECT OF DEOXYGENATION RATE ON OXYGEN SAG CURVE

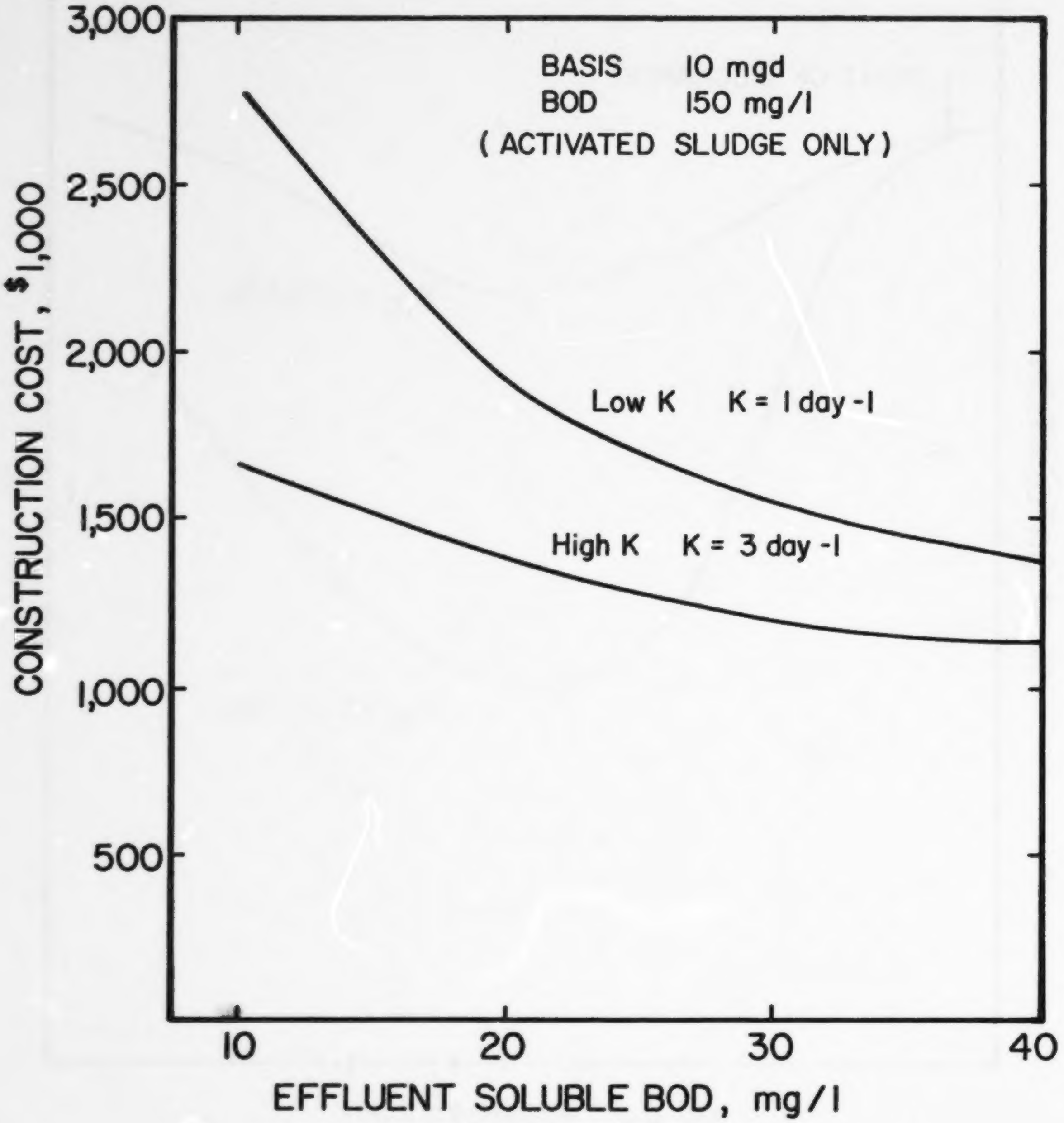

FIG. 2. EFFECT OF BIODEGRADABILITY ON ACTIVATED SLUDGE COSTS

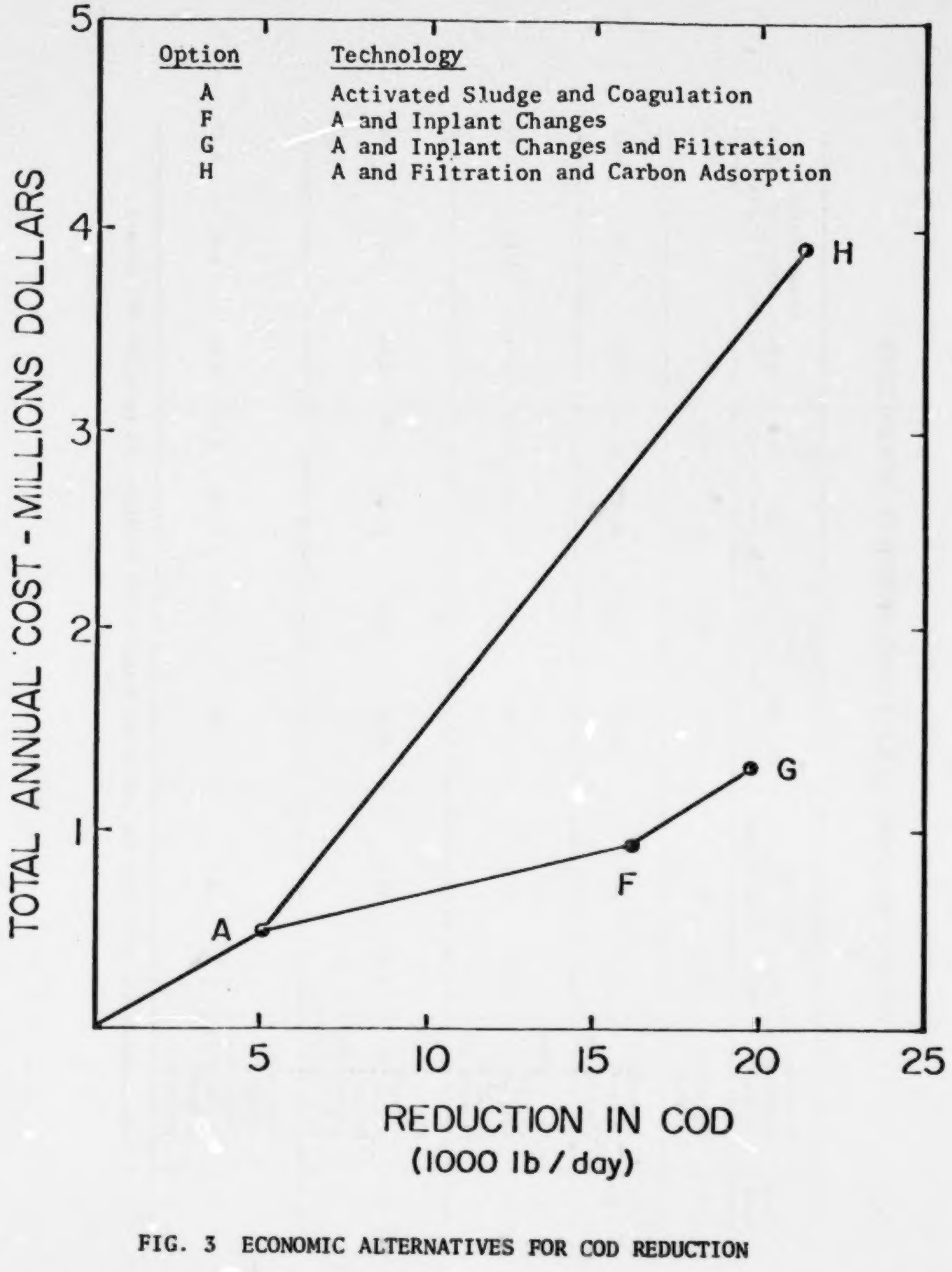

FIG. 3 ECONOMIC ALTERNATIVES FOR COD REDUCTION

TABLE 2 "EFFLUENT QUALITY COST EFFECTIVE ALTERNATIVES"

Graph Code	Pollution Reduction Scheme	Influent to Treatment		Effluent from Treatment				Annual Costs* Millions of Dollars		
		Flow (MGD)	Sol. BOD_5 (1000 lb/day)	Sol. BOD_5 ←	Tot. BOD_5 (1000 lb/day)	COD	TSS →	Capital	Operating	Total
BPT	Activated Sludge	11.1	55.7	3.50	6.30	41.78	8.51	----	----	----
A	Activated Sludge & Coagulation	11.1	55.7	3.50	5.00	36.33	4.62	0.21	0.22	0.43
F	All in-plant changes & Activated Sludge & Coagulation	8.3	37.1	2.35	3.50	25.43	3.46	0.71	0.22	0.93
G	All in-plant changes & Activated Sludge & Coagulation & Filtration	8.3	37.1	2.35	2.81	22.52	1.38	0.93	0.40	1.33
H	Activated Sludge & Coagulation & Filtration & Carbon Adsorption	11.1	55.7	2.27	2.57	17.85	0.92	1.20	2.90	4.10

* Costs presented are those above the cost of the installed BPT facility. All costs are 1975 dollars.

"TREATMENT COST-EFFECTIVENESS AS A FUNCTION OF EFFLUENT QUALITY"

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INTRODUCTION

The cost of required wastewater treatment is a major concern to industry and the petroleum refining industry is no exception. By July 1, 1977, all petroleum refineries in the United States are required to have, as a minimum, treatment technology that will provide an effluent of the quality which the U.S. Environmental Protection Agency (EPA) has defined as "Best Practicable Control Technology Currently Available" (BPCTCA). Five years later, unless the Congress acts to modify Public Law 92-500, the next level of treatment technology, designated as "Best Available Technology Economically Achievable" (BATEA), will be required. In the interim period, effluent limitations for certain toxic constituents in wastewaters, probably including petroleum refining effluents, will be promulgated by EPA under the auspices of Section 307 of Public Law 92-500. Thus, the petroleum refining industry will be required to implement even more costly methods of wastewater control than those which have been applied to date.

This paper addresses the costs associated with the end-of-pipe treatment processes which are most frequently associated with petroleum refinery secondary and tertiary wastewater treatment. The objective is to provide a frame of reference for evaluating treatment costs as a function of increasingly stringent effluent quality limitations. As such, the information presented herein is not all-inclusive in terms of either the costs of reaching a given effluent quality or the end-of-pipe treatment processes considered. Because each refinery has different wastewater problems, it is impossible to accurately assess the effectiveness and cost of in-plant controls for reducing or eliminating raw waste load. Therefore, these costs are not included in this analysis. Furthermore, to simplify the evaluation and allow comparison of these costs with costs in other industrial categories and between individual petroleum refineries, it is assumed that the costs are based on treatment units following primary and secondary oil/solids separation. Finally, a cost comparison of various treatment alternatives at a given level of effluent quality is not the subject of this paper, but it should be recognized that in a specific case at a particular refinery, there may be several options for biological treatment and effluent polishing which should be considered in order to select the least-cost alternative.

All costs shown in this paper are adjusted to January 1, 1977. An annual inflation rate of six percent was used to perform this adjustment and it is recognized that this may be too conservative in some cases. To determine the annual cost of capital, an interest rate of 10 percent amortized over 15 years is used. No attempt was made to adjust the costs presented in this paper for other considerations such as geographical location, the availability of existing land, and similar factors. Reports which have been prepared on the costs of wastewater treatment in the petroleum refining industry have addressed these considerations in depth (Ref. 1, 3) and, while their importance is recognized, their exclusion from this analysis will not affect attainment of the paper's stated objective which is to provide a framework for evaluating cost as a function of effluent quality. It must be emphasized, however, that the costs presented herein are to be used only to provide order of magnitude comparisons of one level of treatment with another and may vary substantially at given petroleum refineries.

The remainder of this paper is organized into two main sections: the first presenting limited cost information from petroleum refining and petrochemical waste treatment facilities which are considered representative for a cost comparison of this type; and the second being an analysis of the costs associated with a model refinery which is used as an example to illustrate the increasing costs as the effluent quality limitations become more stringent. The cost comparisons presented in this paper are presented on a unitized basis using both the flow of the wastewater being subjected to treatment and the removal of pollutants associated with each of the unit processes. This is a useful way to evaluate cost data inasmuch as it demonstrates unit process cost-effectiveness not only in terms of the quantity of wastewater treated, but also in terms of the removal of pollutants which it is designed to treat.

The three levels of end-of-pipe control technology which are addressed in this paper are biological treatment, as represented primarily by the activated sludge process for petroleum refinery wastewaters, effluent polishing for suspended solids removal which is represented by granular-media filtration, and tertiary effluent polishing which is represented by activated carbon adsorption in columns or beds. In addition, cost data are presented for the model refinery for removal of selected potentially toxic pollutants which may occur in petroleum refinery wastewaters.

INDUSTRIAL CASE HISTORIES

Industrial case history data for three levels of effluent control are presented in the following sections: biological treatment, granular-media filtration of biologically treated effluents, and activated carbon treatment of selected industrial wastewaters. These cost data, which are primarily for petroleum refining applications, are presented to give the reader an idea of the range of costs which might be encountered for treating petroleum refining wastewaters to each of the effluent quality levels which can be assumed to be approximated by the end-of-pipe treatment technology described above.

Biological Treatment

Table 1 presents cost data for six petroleum refinery case histories utilizing biological treatment. As described previously, these costs represent the biological treatment module only and in all cases the treatment process has been preceded by an air flotation unit for secondary oil/solids removal. The only solids handling costs included in Table 1 are for aerobic digestion and thickening of waste activated sludge.

Two basic types of biological treatment systems are shown; completely mixed activated sludge and rotating biological surface (RBS). Other biological processes which might achieve similar levels of effluent quality, the most notable of which for petroleum refining wastewaters is the aerated lagoon, are not included because either insufficient data are available or it would be difficult to make a proper comparison between the process and the two processes shown in Table 1. The aerated lagoon falls into the second category because it is extremely land-intensive and also cannot be assured of continually meeting the level of effluent suspended solids provided by the activated sludge and RBS systems. This is not to say that the aerated lagoon would not provide the necessary effluent quality and be the most cost-effective system for biological treatment at some petroleum refineries.

The cost data for the biological treatment processes shown in Table 1 are largely self-explanatory. However, several interesting conclusions can be drawn from reviewing these data. First, there is suprisingly little variation in the cost, in $/1000 gal, of biological treatment of petroleum refining wastes considering the rather significant size and raw waste load differences between the petroleum refineries. There is an obvious economy-of-scale as a function of flow for both the activated sludge and RBS systems. The influence of organic raw waste load on both the capital cost and operation and maintenance (O&M) costs of biological waste treatment is demonstrated by these data.

It must be recognized that there are several factors which influence the cost-effectiveness of biological treatment for a particular petroleum refining or other industrial waste. One factor is the size of the facility in terms of both quantity of wastewater treated and raw waste load. There is substantial economy-of-scale in biological waste treatment systems at both higher flow rates and higher organic loadings. Another important factor in determining the costs of biological waste treatment is the biological kinetics for the particular wastewater being treated. A wastewater with a high organic removal rate requires a relatively smaller aeration basin but may also require higher aeration capacity than a wastewater with a lower removal rate. These factors have obvious influences on both capital and operating costs. Thus, it must be recognized that the unit costs shown in Table 1 are subject to both increases and decreases, depending upon the specific characteristics of a particular petroleum refinery wastewater and the design of the biological treatment facility.

Effluent Suspended Solids Removal

The next step in end-of-pipe treatment usually considered following biological treatment is enhanced suspended solids removal. In some cases, biological treatment systems for petroleum refinery wastewaters have consistently demonstrated effluent suspended solids concentrations in the range of 15 to 10 mg/l. This, however, is the exception rather than the rule. At most refineries utilizing activated sludge plants, an average effluent total suspended solids (TSS) concentration in the range of 30 to 40 mg/l can be expected. Tertiary effluent polishing consisting of either polishing ponds or granular-media filtration is common for decreasing effluent suspended solids concentrations. The polishing ponds cannot be considered as an option which will work in all cases; therefore, only the granular-media filter systems are considered in this cost analysis. The filters are designed mainly to remove TSS, however, organic materials, as measured by five-day BOD and COD, representing the organic content of the solids removed by the filters, are also removed. In addition to this improvement in effluent suspended solids content and organic content, polishing filters can be considered a requirement prior to further effluent polishing by activated carbon adsorption or more exotic processes such as reverse osmosis.

Table 2 shows case history cost data for two different industrial installations of biological effluent polishing. These costs represent comparisons of different types of granular-media filtration systems used at the two industrial plants. The unitized capital costs reflect a large economy-of-scale engendered by the great difference in size between the two facilities in terms of both the quantity of wastewater treated and the pounds of suspended solids removed. The annual O&M costs also reflect the economy-of-scale, but to a lesser extent than the capital costs. The unitized costs are reasonably low in terms of quantity of wastewater treated and pounds of suspended solids removed, at least for the larger filtration system. However the effectiveness of a filtration system for removing organic material is quite poor, as is reflected by the high cost per pound of five-day BOD removed in the filtration system. Thus, it can be concluded that the filters are a good unit process for removing suspended solids if suspended solids are considered a serious pollutant. On the other hand, the cost-effectiveness of the filters in removing organic materials is very poor, as might be expected, and an alternative would be to design the biological system to remove more of the organics, if this is feasible, rather than using the filtration system to remove organics.

Tertiary Organics Removal

The remanded 1983 guidelines for the petroleum refining industry were based on the use of activated carbon adsorption to remove additional organic constituents from biologically treated petroleum refining effluents. The intention was to remove those organic compounds which pass through the biological treatment system, as measured by COD and total organic carbon (TOC), and which might either exert a long-term oxygen demand or create chronic toxicity in the receiving waters. Recently, it has been suggested that the primary application of activated carbon might be as pretreatment for selected wastewater streams within a plant to reduce refractory or potentially toxic organic compounds at the source. Notwithstanding this possible future change in application for activated carbon, there is still emphasis by the EPA on the use of carbon adsorption technology as part of BATEA effluent treatment. Unfortunately, no full-scale operating data are currently available for carbon adsorption technology in the petroleum refining industry. Table 3 provides some unitized cost information for the use of activated carbon treatment technology in several applications including the only two full-scale plants in the petroleum refining industry. None of the unit costs presented in Table 3 are directly comparable. They represent different types of treatment systems and different wastewaters. The two petroleum refining systems include the continuous carbon columns at the BP petroleum refinery in Marcus Hook, Pennsylvania which treat refinery wastewaters that have been pretreated by gravity separation and granular-media filtration. Biological pretreatment is not included in this system. The second petroleum refinery system is at the ARCO refinery in California. This system operates on an intermittent basis without biological pretreatment and consists of fixed beds which are used for organics removal from mixed storm and process wastewaters. The third set of unit costs shown in Table 3 are estimates prepared for a tertiary carbon system following biological treatment of mixed industrial wastewaters, including petroleum refinery wastes. The costs presented for the above three facilities exclude the costs of pretreatment systems. The final two sets of unitized costs shown in Table 3 are for the use of powdered activated carbon in activated sludge aeration basins. Obviously, the level of effluent quality attainable with these latter two systems is not comparable with that of the former three, but since this application is receiving considerable attention, it was included in this Table.

Given the basis of the data provided for the activated carbon systems in Table 3, only general comparisons can be made. However, it is easy to see that the cost-effectiveness in terms of both quantity of watewater treated and pounds of organic materials removed is much poorer for the activated carbon systems than it is for biological treatment. This is not unexpected considering the fact that the activated carbon systems are both energy and labor intensive and the carbon itself is quite expensive. In the tertiary polishing application, the quantity of five-day BOD and COD removed is relatively small compared to that removed in the biological treatment phase which tends to make the unit costs of removal much higher. This phenomena is expected and, as will be demonstrated in the next section, makes the cost of this level of effluent treatment quite high in terms of cost per unit of pollutant removed.

MODEL REFINERY COST ANALYSIS

The preceding sections illustrated how the unit cost of waste treatment increases substantially as the effluent quality limitations become increasingly more stringent over a rather narrow range in terms of the commonly used parameters. Since these costs reflect a wide range of waste characteristics, specific plant characteristics, and other similar factors which result in the rather wide ranges demonstrated by these data, it is useful to prepare an example analysis for a specific petroleum refinery to observe how treatment cost-effectiveness relates to effluent quality. This is accomplished by creating a hypothetical petroleum refinery, referred to hereinafter as the "Model Refinery," of a given size and with specified wastewater characteristics and then preparing cost estimates for increasingly stringent levels of end-of-pipe control. It is reemphasized that the costs presented in this paper include only end-of-pipe treatment and exclude costs associated with in-plant control and the pretreatment system prior to biological treatment. The costs of solids handling, which are always significant, are not included in this analysis.

The Model Refinery selected for the cost-effectiveness analysis is the Subcategory B, median refinery which was used in a study for the National Commission on Water Quality (Ref. 3). The characteristics of this hypothetical refinery are shown in Table 4. It is emphasized that this refinery is strictly hypothetical and does not represent any actual refinery.

The wastewater characteristics at varying levels of treatment for this Model Refinery are shown in Table 5. The values indicated in this Table can be considered annual average concentrations and flows. This Table shows the expected levels of effluent quality which will be obtained by the application of biological treatment, tertiary filtration, and tertiary carbon adsorption. These concentrations are used as the basis for the cost-effectiveness analysis. In Table 6, the incremental mass of pollutant removed by each of the three end-of-pipe treatment processes being considered is shown. It is obvious that biological treatment removes the majority of the organic materials from the petroleum refinery wastewater and the additional levels of treatment, including tertiary filtration and carbon adsorption, remove relatively small quantities. This impacts heavily on their cost-effectiveness.

The capital costs, annual O&M costs, and annual energy costs for each of the three incremental levels of end-of-pipe treatment for the Model Refinery wastewater were calculated using cost data from a recent study conducted for the State of Texas. These costs are shown in Table 7. The annual O&M costs shown in Table 7 do not include the cost of energy, which is shown separately. These costs can be considered to be planning-level cost estimates for the Gulf Coast area.

The data on the size and performance of the Model Refinery wastewater treatment plant presented in Tables 5 and 6 can be used with the cost data in Table 7 to analyze the cost-effectiveness for each of the three levels of end-of-pipe treatment. These unit costs, presented in terms of quantity of wastewater treated and pounds of specified pollutant removed, are presented in Table 8. To obtain the total annual cost for a given end-of-pipe treatment system and a selected basis, i.e., flow, BOD, etc., the two figures shown as capital and annual O&M costs can be summed. To facilitate comparison of the cost data shown in Table 8, several Figures have been prepared. Figure 1 shows the total annual cost of end-of-pipe wastewater treatment as a function of annual average effluent five-day BOD concentration. The unit costs in terms of both flow and five-day BOD removal are shown in this Figure. In terms of unitized costs as a function of flow, the cost increase between activated sludge and granular-media filtration is approximately 40 percent. The same increment, when viewed in terms of additional five-day BOD removal, represents an approximate sixfold increase in unit cost. As might be expected by the low incremental removals of BOD shown in Table 6 and the high cost of treatment shown in Table 7, the activated carbon adsorption unit results in an almost exponential increase in cost for a 10 mg/l improvement in effluent five-day BOD concentration. However, since the activated carbon unit is primarily designed to remove materials which are not easily biologically degraded, its effectiveness is better viewed in terms of COD removal, as shown in Figure 2. Once again, the unit cost of COD removal increases very rapidly as treatment beyond the biological step is implemented. A threefold decrease in effluent COD concentration between biological treatment and activated carbon levels of effluent control technology results in an approximate tenfold increase in total annual cost, expressed as $/lb COD removed. Figure 3 expresses the cost data shown in Figures 1 and 2 in a slightly different manner, showing the cumulative total annual cost expressed as $/lb BOD or COD removed as a function of percent removal of BOD and COD from the pretreated refinery wastewater. Once again, this Figure shows the almost exponential increase in cost associated with the removal of a small increment of BOD going from biological effluent to the activated carbon system, whereas it shows an almost linear increase in the cost of COD removal as a function of percent removal.

Figure 4 presents the total annual costs of end-of-pipe waste treatment at the Model Refinery from a different perspective than that presented in the preceding Figures and Tables. This Figure illustrates the actual cumulative total annual costs for end-of-pipe waste treatment for the Model Refinery and shows the distribution of these costs between O&M and the cost of capital for each type of facility. This is simply a graphical representation of the costs shown in Table 7 but illustrates effectively some interesting relationships not shown by the unitized costs. The addition of granular-media filtration to an activated sludge system results in about a 35 percent increase in total annual cost for the end-of-pipe treatment system excluding primary and secondary oil/solids removal. Most of this cost is associated with the capital costs of the filter system as the increase in annual operation and maintenance costs due to the filter is only about 10 percent of the same costs for the biological system alone. When the carbon adsorption step is added for removal of refractory organics, however, the O&M costs actually exceed the annual costs for amortizing the capital investment in the activated carbon units. This is brought about principally by the energy costs associated with carbon regeneration and the cost of purchased carbon for makeup of system losses. The increase in total annual costs due to the addition of the carbon system is about 390 percent of the cost of the biological system alone but is a far smaller percentage increase than if the costs are considered on a unitized basis, as illustrated in Figures 1 through 3. This serves to reemphasize the point made earlier: the capital costs of implementing the carbon technology for polishing of biological effluents are not significantly greater than the cost for biological treatment plus filtration and are less than the overall costs of meeting BPCTCA effluent quality. However, the cost of this level of treatment per unit of pollutant removed is many times that of the biological system and the petroleum refineries will pay dearly for every mg/l of COD removed by this method. This raises very strongly the question of whether or not the uniform application of carbon adsorption technology to polishing biological effluents is a necessary and cost-effective requirement for meeting the quality standards set for our nation's waters.

The preceding cost evaluations have dealt with the end-of-pipe treatment systems which will be used in petroleum refineries to remove organic substances measured as BOD, COD, and suspended solids. An extremely important consideration over the next several years will be the impact on the petroleum refining industry of the toxic effluent limitations which are currently being prepared by EPA in accordance with Section 307 of Public Law 92-500. In a consent decree from the Circuit Court of Appeals in Washington, D.C., the EPA agreed to promulgate toxic effluent limitations for selected constituents from a list of some 65 different classes of compounds. As of the date of this paper, some 109 different chemical compounds are being studied in detail to determine whether or not toxic limitations should be promulgated under Section 307. Since these limitations have not yet been promulgated, an evaluation of the cost-effectiveness of the associated treatment technology is not possible at this time. However, as an example, several constituents which may be found in petroleum refinery wastewaters can be used to evaluate cost-effectiveness of treatment processes designed for specific constituent removal.

Cadmium, cyanides, and chromium can be found in some petroleum refinery wastewaters and can be toxic to certain organisms in the receiving waters if they are discharged at high enough concentrations. There is, however, considerable controversy as to the toxic concentrations of many of these materials and the selection of these for an example cost-effectiveness analysis is not to be construed as suggesting that the limitations selected for the performance of treatment processes to remove these constituents represent their toxic concentrations in receiving waters.

Cadmium is not present in most crude oils; therefore, the source of cadmium in petroleum refinery wastewaters is either intake water or cadmium addition during processing (Ref. 3). Cadmium in petroleum refinery wastewaters can generally be traced to intake water, corrosion products, the addition of cadmium compounds for distillate desulfurizing, or as a lube oil additive to prevent oxidation. Because of the diffuse nature of the cadmium sources in petroleum refineries, it is not generally practical to attempt to segregate cadmium-bearing waters for separate treatment. Thus, for the Model Refinery used in the cost analysis, treatment for removal of cadmium involves treatment of the entire process wastewater effluent. Lime precipitation and filtration is probably the most dependable method of removing cadmium. Cadmium forms an insoluble and highly stable hydroxide precipitate at an alkaline pH and, in the absence of appreciable complexing agents, precipitation and filtration provide effective removal. The completeness of the reaction is a function of pH and lime addition to pH 10 is required to meet the concentration limit selected for this evaluation, which is 0.05 mg/l. The cadmium removal process selected requires provisions for lime addition, rapid mix, flocculation, sedimentation, filtration, and reneutralization to pH between 6 and 9. Table 9 shows the total annual costs, the amortized capital costs, and the annual O&M costs for removing cadmium from the Model Refinery wastewater stream of 1.0 MGD. The total annual cost of $0.40 per 1000 gallons is approximately two-thirds due to O&M costs, most of which are associated with the purchase of lime, and one-third due to the amortized capital costs. No cost per pound of cadmium removed can be calculated for this process because of insufficient information on cadmium concentrations in petroleum refining effluents. However, it is known that these concentrations are generally quite low, and thus the cost per pound of cadmium removed is likely to be extremely high.

Simple and complex cyanides are generated in cracking and coking operations as reaction products and enter the effluent from overhead receivers and through washing operations (Ref. 3). Most or all of the cyanide generation in a refinery occurs in these two operations, so the cyanide-bearing water can generally be isolated from other waste streams within the refinery complex and treated separately. Alkaline chlorination is the most proven treatment technology for removing cyanides from wastewaters although its application in the petroleum refining industry has not been extensively tested (Ref. 3). Cyanides can be reduced to less than 0.025 mg/l with appropriate pH control, chlorine dosage, and residence times. Biological treatment of refinery wastewaters is quite effective in reducing cyanides to concentrations below 0.5 mg/l, however, for the purposes of this cost-effectiveness analysis it is assumed that alkaline chlorination will be required to produce a final effluent concentration of approximately 0.025 mg/l total cyanides. In the

Model Refinery this will be accomplished by segregating the sour water streams, after stripping, from the fluid catalytic cracker and coker and subjecting them to alkaline chlorination. The total estimated quantity of the wastewaters requiring treatment in the model refinery is 150,000 gpd, containing approximately 100 mg/l of total cyanides. The annual costs associated with treatment of these waste streams in the Model Refinery to remove cyanides are shown in Table 9. The capital costs of the cyanide removal system are quite low, since the only equipment items required are a chlorinator, reaction tank, and a caustic feed system. However, the annual O&M costs per 1000 gallons of waste treated are extremely high, resulting in a total annual cost of $2.24 per 1000 gallons. In terms of total annual cost per pound of cyanide removed, the cost-effectiveness of this unit operation is even poorer, resulting in a cost of $2.68 per pound of cyanide removed on an annual basis. The majority of the costs for this process are associated with the neutralization chemical, sodium hydroxide, and the chlorine. Another potential drawback of this process which should be mentioned is the possible formation of chlorinated hydrocarbons which, of themselves, may prove to be toxic materials.

The final specific constituent considered for removal is chromium. The major source of chromium within petroleum refineries is the chromate-based corrosion inhibitors used in cooling towers. These inhibitors find their way to the wastewater treatment plant in cooling tower blowdown. Chromium is included in the effluent limitations for the petroleum refining industry which have been promulgated by EPA, but it is also being considered under the toxic effluent limitations being reviewed at this time. In petroleum refineries, the effluent chromium limitations can usually be met without resorting to separate treatment of cooling tower blowdown. However, in many other types of industrial plants, particularly in the organic chemicals industry, cooling blowdown constitutes a very high volume and is not treated in the biological waste treatment plant. In these cases, it is often necessary to remove chromium from the cooling tower blowdown before it is discharged to the receiving waters and several treatment methods have seen wide application. The types of treatment technology used for removing chromium from cooling tower blowdown include chemical reduction/precipitation, ion exchange, and electrolytic reduction/precipitation. Each of these treatment processes has advantages and disadvantages. The electrolytic process is finding increasing applications for treating cooling tower blowdown and is used in this example cost analysis for the Model Refinery. It is assumed for the purposes of this example that the Model Refinery generates approximately 190,000 gpd of cooling tower blowdown which is treated by the electrolytic reduction/precipitation method. The costs of applying this treatment procedure are shown in Table 9. The total annual cost for chromium removal by this method for this size facility is approximately $0.66 per 1000 gallons, but is $4.06 per pound of chrome removed. This assumes an influent chromate concentration in the cooling tower blowdown of approximately 20 mg/l and an effluent concentration from the unit of approximately 0.5 mg/l of chromate.

SUMMARY

This paper has presented an evaluation of the cost-effectiveness of several important processes in petroleum refinery wastewater treatment using both actual cost data from full-scale facilities and an example cost analysis for a hypothetical petroleum refinery. The salient points of this evaluation can be enumerated as follows:

(1) Cost-effectiveness, expressed on a unit cost basis as a function of effluent quality, should be based upon the constituent or constituents of the wastewater which are to be removed by the waste treatment process being evaluated, if the most meaningful comparisons are to be made.

(2) In terms of removal of organic materials from petroleum refinery effluents, biological treatment is by far the most cost-effective. Suprisingly, multimedia filtration is the second most cost-effective, and tertiary effluent polishing with carbon adsorption is the least cost-effective of the likely alternatives for this application.

(3) The poor effectiveness of carbon adsorption technology when used on a biologically treated effluent for the purpose of removing trace refractory materials raises a serious question as to whether this is the most suitable application for this treatment process. In the absence of known specifically toxic organic constituents, questions should be raised about the efficacy of removing trace residual organics, as measured by COD or TOC, simply for the purpose of reducing the effluent concentrations unless there is a concommitant improvement in receiving water quality. This particular point was made quite effectively by Mr. Joe Moore at last year's Open Forum. At that time he indicated that the cost-effectiveness of BATEA technology should be carefully considered before requiring nationwide implementation (Ref. 6).

(4) The cost-effectiveness of unit processes designed for the removal of specific constituents in petroleum refining waste streams will probably be quite poor in terms of unit cost per quantity of wastewater treated or constituent removed. This is not unexpected, however, and, if a constituent is truly toxic at the effluent concentrations being considered, the unit cost of removing the constituent has no real meaning since Public Law 92-500 precludes discharge of toxic materials in toxic quantities.

(5) Expressing the performance of various waste treatment unit processes in terms of unit costs per quantity of flow treated or mass of constituent removed is an effective basis for cost comparisons between alternative unit processes. It is a convenient method for putting costs of treatment processes designed to perform a given service on a consistent basis and allows a direct comparison of the respective costs of each option.

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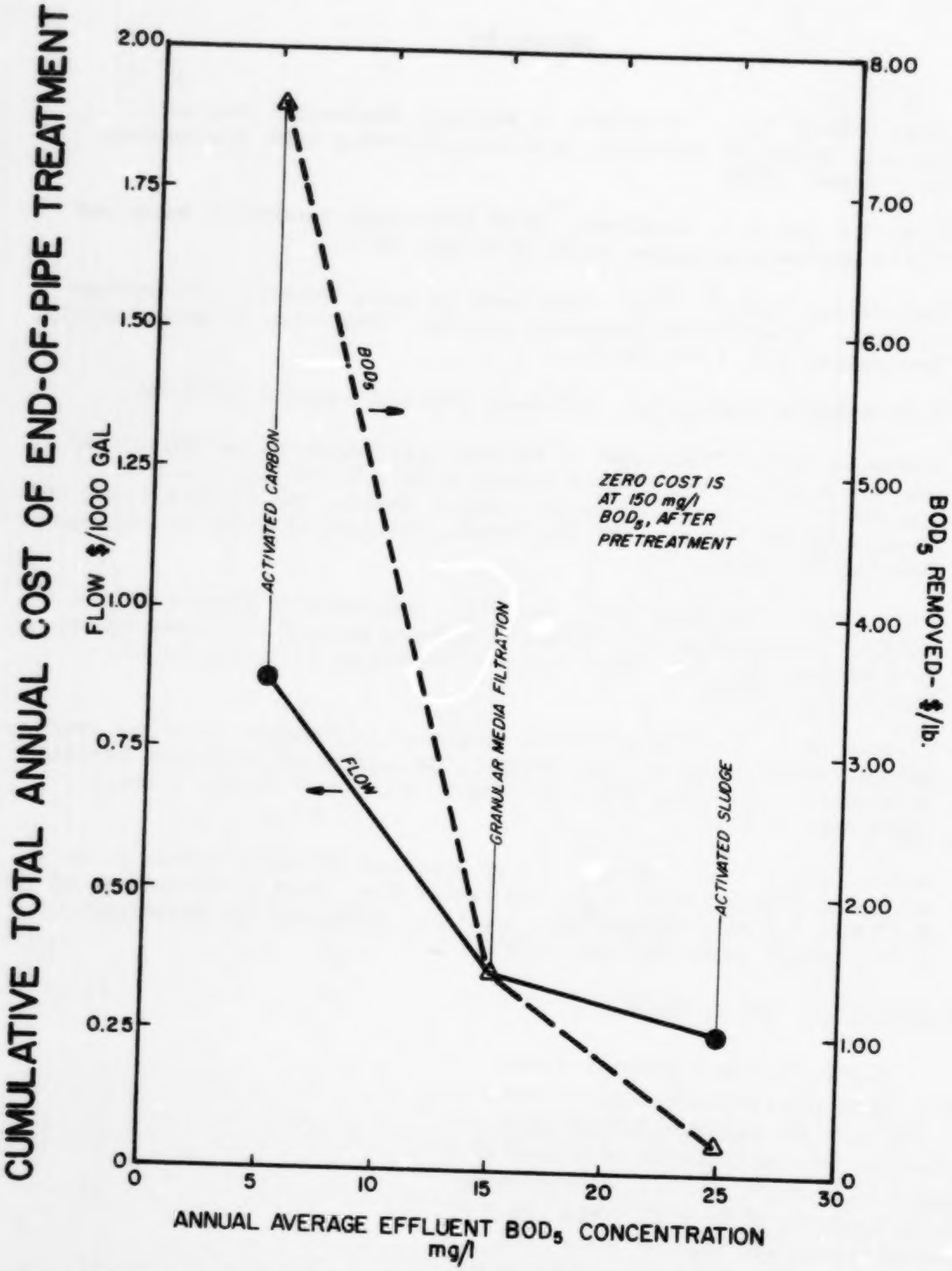

Fig.1 TOTAL ANNUAL COST OF WASTE TREATMENT–
MODEL REFINERY

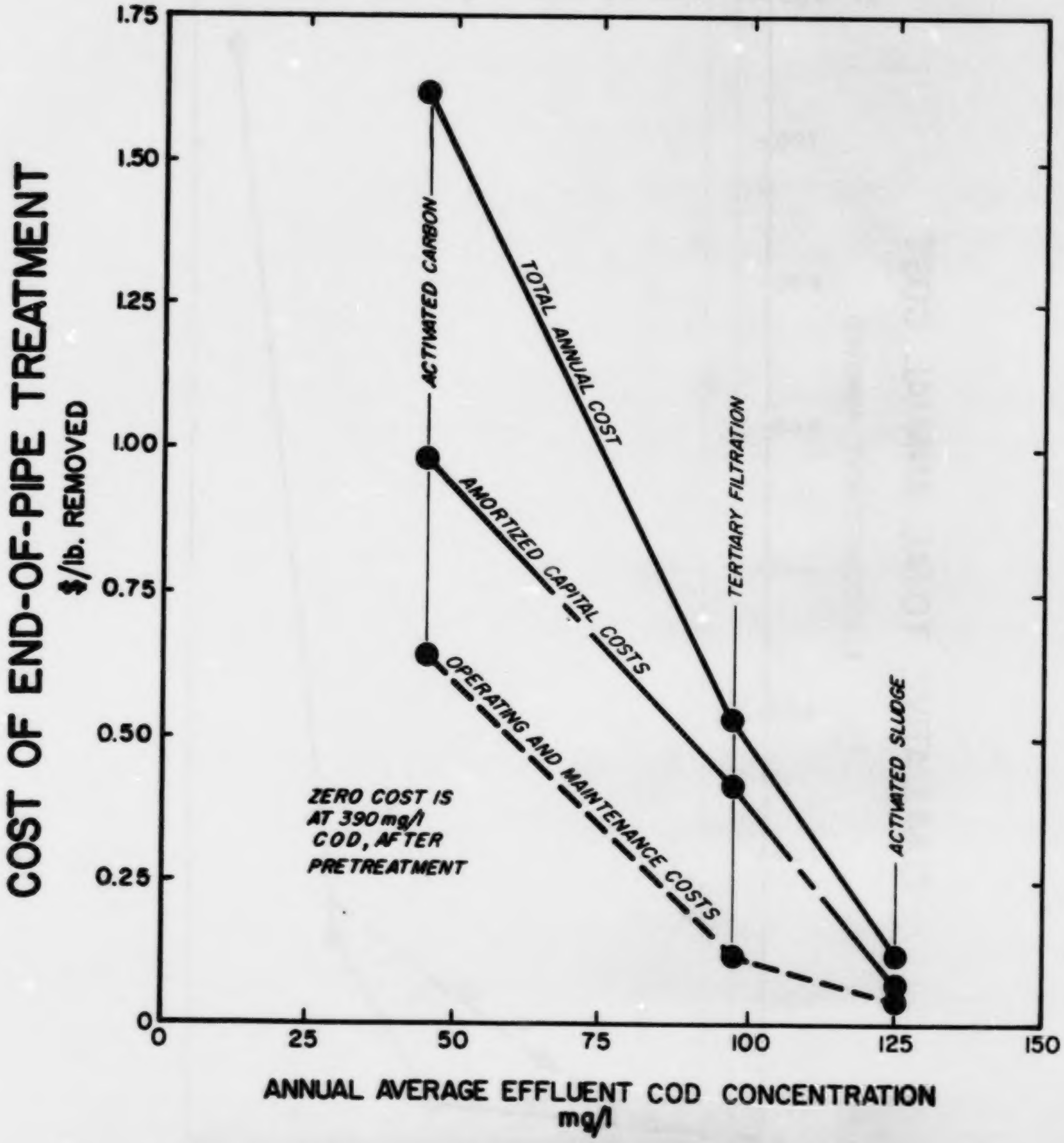

Fig.2 COST OF WASTEWATER TREATMENT FOR MODEL REFINERY AS A FUNCTION OF EFFLUENT COD

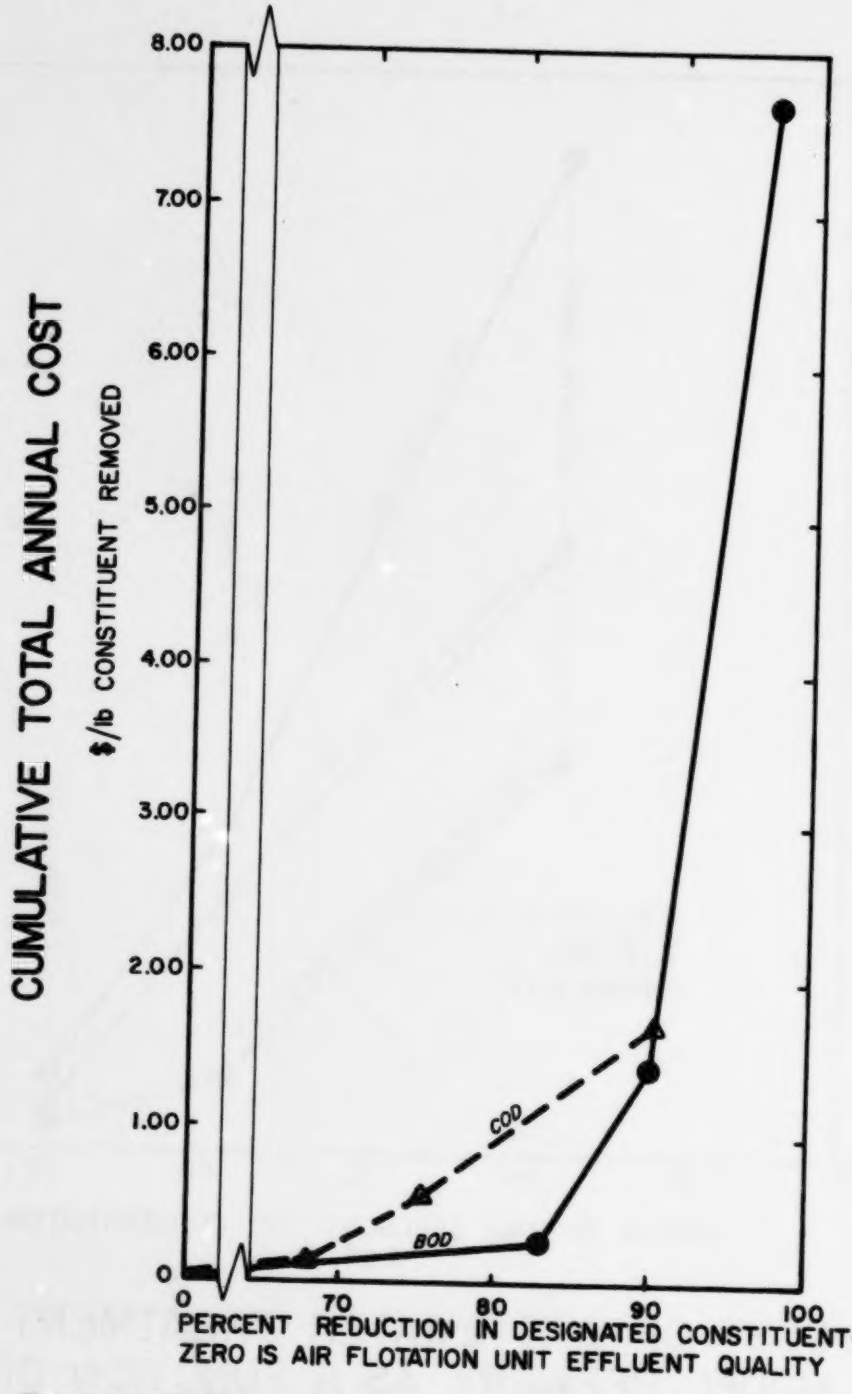

Fig.3 UNITIZED TOTAL ANNUAL COST OF WASTE TREATMENT AS A FUNCTION OF REMOVAL EFFICIENCY-MODEL REFINERY

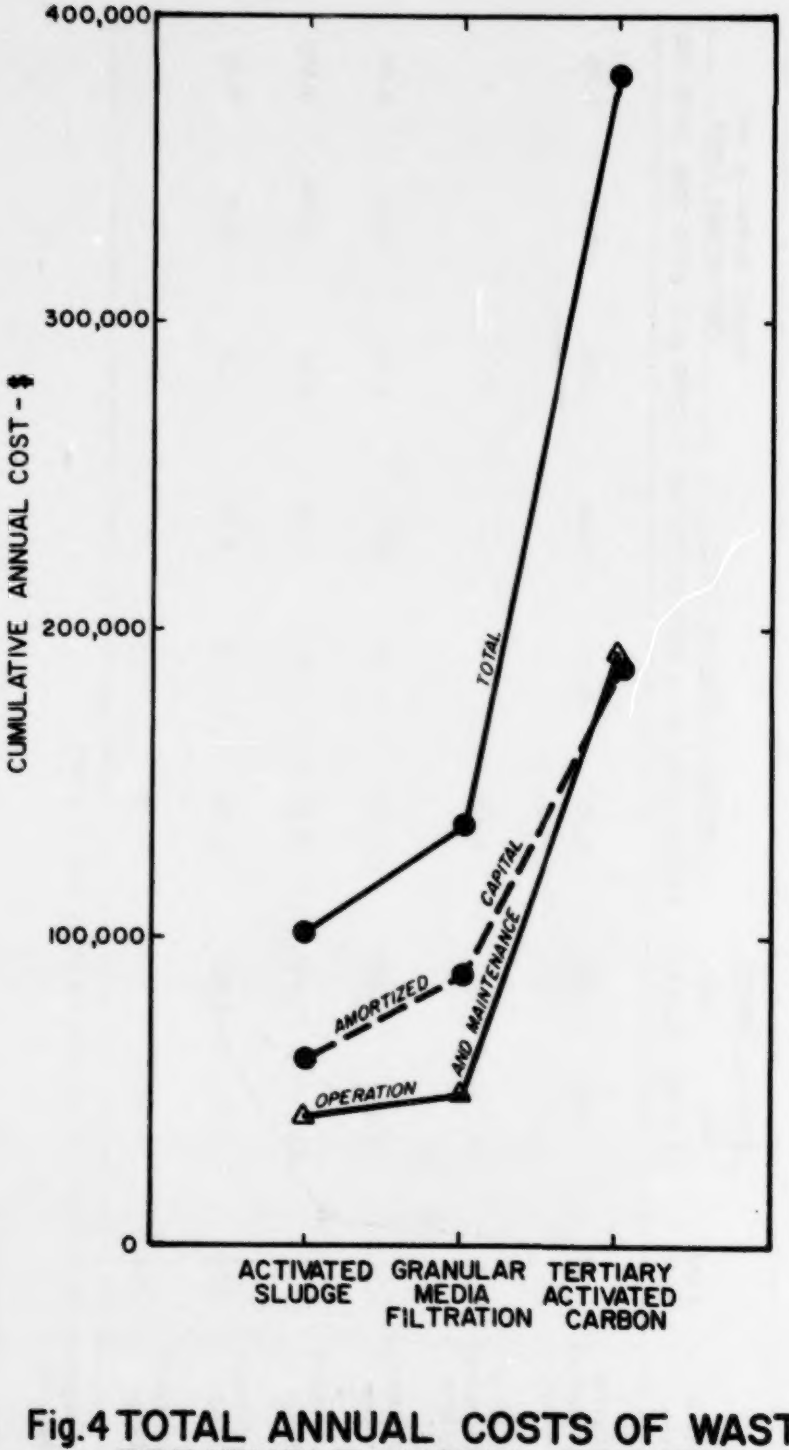

Fig.4 TOTAL ANNUAL COSTS OF WASTE TREATMENT - MODEL REFINERY

TABLE 1

CASE HISTORIES OF BIOLOGICAL TREATMENT AT PETROLEUM REFINERIES

System Type	Flow (MGD)	Organic Removal		Amortized Capital Cost*			Annual Operation and Maintenance Costs		
		BOD_5 (lb/day)	COD (lb/day)	($/1000 gal)	($/lb BOD)	($/lb COD)	($/1000 gal)	($/lb BOD)	($/lb COD)
Rotating Biological Surface	0.9	840	1,200	0.23	0.24	0.16	0.06	0.12	0.05
Rotating Biological Surface	4.3	5,300	-	0.19	-	-	-	-	-
Activated Sludge	4.6	9,100	26,200	0.12	0.06	0.02	0.10	0.05	0.02
Activated Sludge	3.9	41,500	83,000	0.19	0.02	0.01	0.07	0.006	0.003
Activated Sludge	1.9	8,600	13,000	0.24	0.05	0.03	0.12	0.03	0.02
Activated Sludge	2.3	3,100	-	0.19	0.14	-	-	-	-

* Adjusted to 1977 and 10 percent interest for 15 years.
(Ref. 4)

METRIC CONVERSIONS

1/sec = (MGD) (43.81)
kg = (lb)(0.454)
1000 liters = (1000 gal)(3.785)

TABLE 2

INDUSTRIAL CASE HISTORIES OF TERTIARY GRANULAR-MEDIA FILTRATION

Type Filter System	Flow (MGD)	Solids Removal (lb/day)	Amortized Capital Cost*			Annual Operation and Maintenance Costs		
			($/1000 gal)	($/lb TSS)	($/lb BOD)	($/1000 gal)	($/lb TSS)	($/lb BOD)
Downflow Deep Bed	1.44	240	0.19	1.15	3.83	0.07	0.41	1.37
Downflow Shallow Bed	1.44	240	0.14	0.85	2.85	0.06	0.34	1.14
Downflow Deep Bed Gravity	48.5	24,269	0.05	0.11	0.36	0.04	0.07	0.22
Downflow Deep Bed Pressure	48.5	24,269	0.07	0.13	0.44	0.03	0.07	0.22
Tri-media Gravity	48.5	24,269	0.04	0.08	0.28	0.03	0.07	0.22
Tri-media Pressure	48.5	24,269	0.04	0.09	0.29	0.03	0.06	0.19

* Adjusted to 1977 and 10 percent interest for 15 years.
(Ref. 4)

METRIC CONVERSIONS

1/sec = (MGD)(43.81)
kg = (lb)(0.454)
1000 liters = (1000 gal)(3.785)

TABLE 3

CASE HISTORIES OF INDUSTRIAL ACTIVATED CARBON TREATMENT

System	Flow (MGD)	Organic Removal		Amortized Capital Cost*			Annual Operation and Maintenance Costs		
		BOD_5 (lb/day)	COD (lb/day)	($/1000 gal)	($/lb BOD)	($/lb COD)	($/1000 gal)	($/lb BOD)	($/lb COD)
Petroleum Refinery - (5) Process wastes without biological treatment, continuous columns	2.16	783	2,090	0.31	0.62	0.23	0.134	0.37	0.14
Petroleum Refinery - (7) Storm/process water without biological treatment, fixed beds**	0.85	-	1,311	-	-	-	0.56	-	0.25
Mixed Industrial - (4) Tertiary treatment,*** continuous columns	48.5	5,600	67,550	0.17	1.43	0.12	0.27	2.31	0.19
Petroleum Refinery - (8) Powdered carbon addition to aeration basin	1.08	11	347	None, Manual addition of powdered activated carbon			0.03	2.72	0.09
Municipal - (2) Tertiary powdered activated carbon addition to aeration basin	10.0	-	-	0.08	-	-	0.02	-	-

* Adjusted to 1977 and 10 percent interest for 15 years.

** Intermittent operation.

***Excludes cost of necessary pretreatment by granular-media filtration.

Note: Numbers in parentheses following system description indicate references which can be found at the end of the text.

METRIC CONVERSIONS

1/sec = (MGD)(43.81)

kg = (lb)(0.454)

1000 liters = (1000 gal)(3.785)

TABLE 4

CHARACTERISTICS OF MODEL REFINERY FOR COST-EFFECTIVENESS ANALYSIS

Subcategory B, Cracking

Crude throughput: 42,500 BPSD

METRIC CONVERSION

m^3/day = (0.0159)(BPSD)

Refinery characteristics:

Crude desalting	42,500 BPSD
Atmospheric distillation	42,500 BPSD
Vacuum distillation	16,000 BPSD
Hydrocracking	9,000 BPSD
Fluid catalytic cracking	12,000 BPSD
Coking	2,000 BPSD
Hydrotreating	8,000 BPSD
Catalytic reforming	10,000 BPSD
Asphalt	1,000 BPSD

EPA Configuration: 5.91

(Ref. 3).

TABLE 5

MODEL REFINERY WASTEWATER CHARACTERISTICS AT VARYING LEVELS OF TREATMENT

	Annual Average			
Parameter	After Air Flotation	After Biological Treatment	After Tertiary Filtration	After Tertiary Carbon Adsorption
Flow, $\overline{\text{MGD}}$	1	1	1	1
BOD_5, mg/1	150	25	15	5
COD, mg/1	390	125	97	40
TSS, mg/1	30	40	12	6

(Ref. 3) METRIC CONVERSION 1/sec ≐ ($\overline{\text{MGD}}$)(43.81)

TABLE 6

INCREMENTAL MASS OF POLLUTANT REMOVED BY TREATMENT PROCESS

Parameter	Biological Treatment	Tertiary Filtration	Tertiary Carbon Adsorption
BOD_5, lb/day	1,042	83	83
COD, lb/day	2,210	233	475
TSS, lb/day	-	233	50

METRIC CONVERSION
kg = (lb)(0.454)

TABLE 7

INCREMENTAL COSTS OF WASTEWATER TREATMENT FOR MODEL REFINERY

Treatment Type	Capital Cost	Annual Operation and Maintenance Cost	Annual Energy Cost
Activated Sludge	$ 461,000	$ 32,000	$ 9,000
Tertiary Granular-media Filtration	$ 220,000	$ 6,000	$ 2,000
Tertiary Activated Carbon	$ 740,000	$ 92,000	$ 52,000

Basis: 1977 Gulf Coast Costs.

TABLE 8

INCREMENTAL COST-EFFECTIVENESS OF WASTEWATER TREATMENT FOR MODEL REFINERY

Cost-effectiveness Parameter	Treatment Method		
	Activated Sludge	Tertiary Filtration	Tertiary Carbon Adsorption Columns
Flow, \$/1000 gal			
Capital	0.16	0.08	0.27
Annual O&M	0.09	0.02	0.25
BOD_5, \$/lb removed			
Capital	0.16	0.95	3.20
Annual O&M	0.08	0.20	3.04
COD, \$/lb removed			
Capital	0.07	0.34	0.56
Annual O&M	0.04	0.07	0.53
TSS, \$/lb removed			
Capital	-	0.34	5.31
Annual O&M	-	0.07	5.04

Basis: 1977 Gulf Coast, Capital amortized at 10 percent for 15 years.

METRIC CONVERSIONS
$/1000 liters = ($/1000 gal)(0.26)
$/kg = ($/lb)(2.2)

TABLE 9

COSTS FOR REMOVAL OF SELECTED WASTE CONSTITUENTS FROM MODEL REFINERY EFFLUENT

Waste Constituent	Amortized Capital Cost ($/1000 gal)	Annual O&M Costs ($/1000 gal)	Total Annual Costs	
			($/1000 gal)	($/lb removed)
Cadmium*	0.13	0.27	0.40	-
Cyanides**	0.22	2.02	2.24	2.68
Chromium***	0.23	0.43	0.66	4.06

* Cost based on treating entire refinery process effluent.

** Assumes only FCC and coker process wastes are treated.

*** Assumes treatment of cooling tower blowdown only; 190,000 gpd.

METRIC CONVERSIONS

1000 liters = (1000 gal)(3.785)

kg = (lb)(0.454)

THE ECONOMICS OF HANDLING REFINERY SLUDGES

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The various types of sludges generated in refinery operations may require handling using alternative thickening, stabilization and dewatering processes prior to final disposal. Some or all of these processes may be required depending on the exact nature of the sludge prior to final disposal. Final disposal practices might include landfilling, lagooning, land farming, or incineration of the sludge prior to disposal of ash using one of the above methods. The predominance of each of these disposal methods as it existed in 1973 in an estimate for 1983 conditions is presented in Table 1. These data indicate that landfilling and lagooning are the predominant methods in use at the present time, while it is anticipated that the predominance of lagooning as a disposal method will decrease significantly in the next several years and will be accompanied by a significant increase in the popularity of land farming. Incineration is not expected to be in widespread use in the industry in the foreseeable future.

Due to the large number of alternative processes for handling and disposal sludges, the cost associated with the construction and operation of these processes plays a large role in the selection of optimum sludge handling systems. This paper presents a discussion of the types and characteristics of sludges originating from refinery operations, alternative techniques for handling these sludges, and the costs associated with various process sequences.

SOURCES AND CHARACTERISTICS OF REFINERY SLUDGES

Normal refinery operations generate several major types of sludges which can be classified as follows:

1. Storage tank bottoms.
2. API separator bottoms.
3. Crude desalting sludge.
4. Catalytic solids.
5. Spent clays and coking fines.
6. Solids from utilities operations and biological wastewater treatment systems.

The basic source of many of the solids is the crude oils which contain materials that are present in the oil as taken from the well and which separate during transportation and storage of the crude oil. The solids usually associated with the crude oil include iron rusts, iron sulfides, clay, sand, salt crystals, wax, and paraffin. These solids will generally settle out either in the storage tank bottoms or API separators. Solids from biological treatment of wastewaters are generated when soluble and colloidal biodegradable organics are converted into a biological mass which is separated from the treated wastewater by gravity and concentrated for disposal. The waste sludge from API separators plus typical secondary treatment facilities will contain approximately

1,500 to 2,000 lb of dry solids per million gallons of effluent treated. A delineation of types and characteristics of refinery solids are given in Tables 2 and 3.

Those sludges which pose the major handling and disposal problems to a refinery are from the utilities and wastewater treatment systems. The utilities solids are usually sludges generated from the addition of lime or alum to treat raw water for use in the plant. Since these solids are relatively inert and have no heat content, they should be dewatered and landfilled directly. Sludges gnerated from the wastewater treatment facility include oily sludges from API separators and air flotation systems and biological sludges from trickling filter and activated sludge processes. These solids can be dewatered and incinerated with other combustible solids or disposed of in combination with the utilities and other organic sludges.

The sludges from a refinery which are readily combustible include the waxy bottoms, oil sludges, coke fines, and waxy tailings. The non-combustible sludges are sand, rust, silt, tetraethyl lead sludge, salt, spent catalysts, and lime sludge. The excess biological sludge, although not readily combustible, can be dewatered to an autogenous state.

SLUDGE HANDLING METHODOLOGY

In order to implement a successful sludge management program in a refinery, both in-plant recovery and reclamation of applicable solids combined with final sludge handling and ultimate disposal are required. In-plant management consists of tight operational control, preventive maintenance for leak control and the location of separators at critical points to capture materials before they become contaminated and, thus, uneconomical to recover. Sludge handling methods consist of gravity or air flotation thickening, dewatering by vacuum filtration, pressure filtration, pressure belt filtration, or centrifugation, and final disposal by incinceration, landfill, land farming and barging to sea. Alternative sludge handling methods for oily and biological sludges are shown in Figures 1 and 2, respectively.

There are basically three types of sludges which must be handled by refinery wastewater treatment and sludge handling systems:

1. Recoverable oils.
2. Oily sludges.
3. Biological sludges.

Solids concentrations attainable using various dewatering processes is included in Figure 3. An in-depth discussion of alternative handling methods has been presented elsewhere (2) and, although many refineries handle the oily sludges in combination with the biological sludges, the handling will be presented separately for clarification in this paper. Detailed design procedures for these processes are presented in Reference 4.

Recoverable Oils

Generally, recoverable oils are separated from water mixtures by heating with steam to the range of 150° to 180° F. Chemicals are added and the emulsion is broken into three phases: oil, water, and sludge. The oils are usually recovered, the water sent to the wastewater treatment system, and the sludges discharged into the oily sludge handling system. Separator skimmings, which are generally referred to as slop oils, require treatment before they can be reused, due to the high content of solids and water. Solids and water contents in excess of one percent generally interfere with processing. These slop oils are easily treated by heating to 190° F, retained at this temperature for 4 to 6 hours, then settled for 12 to 24 hours. At the end of the settling period, three layers exist: a top layer of clean oil, a middle layer of secondary emulsions, and a bottom layer of water containing soluble components, suspended solids and oils. Frequently, it is advantageous or necessary to add acid or a specific chemical to destabilize slop oil emulsions. The water layer resulting from this treatment contains higher levels of BOD and COD and must be treated through the biological system prior to discharge. Slop oils are also successfully treated by precoat filtration(2).

Oily Sludges

Oily sludges are derived from oil-water separators, tank bottoms or cleanings, air flotation treatment of wastewaters, and cleaning or dredging from lagoons or oxidation ponds. A major consideration in treating oily sludges is that these materials are generated from various sources and are discharged at irregular intervals. Thus, the sludge composition is highly variable from day to day. Often tank bottoms contain heavy emulsions which require special treatment, and the sludge and skimmings from air flotation systems can present special difficulties in handling also. In many cases, the skimmings from air flotation are sent to a skimmed oil tank from which they may be discharged to landfill or pumped to an oil recovery unit. Chemical treatment is generally necessary for oil recovery.

The most common processes for handling oily sludges are gravity thickening, vacuum filtration or centrifugation dewatering, and disposal by landfill or land farming. A summary of the sludge handling methods used for oily sludges is given in Table 4.

Thickening. Gravity thickening methods are generally utilized for oily sludges. Solids loading rates in the range of 5 to 30 lb/sq ft-day are reported with thickened solids concentrations from 3 to 10 percent. Basically, solids and oils recovery are low from gravity thickeners. Due to the presence of heavy particles in oily sludges, flotation thickening has not been very successful for these sludges. Dissolved air flotation has been successful for thickening froth flotation sludges, but other refinery oily sludges are not deemed practical with this method.

Dewatering. Dewatering alternatives for oily sludges include centrifugation, vacuum filtration, and pressure filtration. Figure 4 presents a schematic of a system being utilized for a number of oily sludges. This two-stage system utilizes a first-stage horizontal solid bowl centrifuge to separate oil from the centrate. In this process the sludge is heated to 180° to 200°F prior to centrifugation. The results of centrifuge testing and experience can be summarized as follows:

1. A vertical solid bowl centrifuge is not recommended for dewatering most oily wastes.
2. A horizontal solid bowl centrifuge followed by a high-speed nozzle or disc centrifuge is best suited for dewatering mixtures of contaminated API bottoms, sludge decant pit material and tank bottoms.
3. A horizontal solid bowl centrifuge dewatering oily sludges is anticipated to recover 75 to 90 percent of the solids in the cake when charged with heated oily sludges. The cake will consist of 1 to 5 percent oil and approximately 50 to 60 percent solids.
4. A high-speed nozzle centrifuge separates 95 to 98 percent of the feed oil in the oily phase and 2 to 5 percent in the nozzle water. Thirty to 50 percent of the feed solids will be removed with the oily phase with the remainder being in two water phases.

A significant number of refineries use vacuum filtration for dewatering oily sludges; and if properly implemented, vacuum filtration renders the solids suitable for direct landfill or incineration. In order to accommodate oily solids, a precoat vacuum filter should be used and the incoming solids should be heated to temperatures greater than 170°F. The major conclusions regarding vacuum filtration of oily sludges are:

1. Increased feed temperature greatly improves vacuum solids performance.
2. Addition of spent clay decreases oil recovery and solids filtration rate.
3. Measured filtration loadings of 0.8 to 3.0 lb/sq ft-hr are required for oil recovery.

A fixed plate, high pressure filter press may be used to dewater many types of oily sludges. Effective breaking of solids-stabilized emulsions is obtained with cake solids in excess of 50 percent of oil concentrations in the range of 5 to 20 percent being observed. Increased filtration temperature has a dramatic effect on cake solids and cake oil concentrations at fixed cycle times. Refinery experience indicates that a definite increase in filtration efficiency is obtained with lime additions. A significant decrease in cake oil content can be obtained by washing the cake with hot water.

Test results indicate that the recovered oil will probably require processing through the high chloride slop system. The water phase has not been found to create any problems in the wastewater system.

A new method of sludge dewatering in the United States employs gravity draining of sludges coupled with pressure filtration applied by mechanical means of rollers and belts. These belt pressure filters are capable of achieving solids content in a range of 12 to 30 percent using polyelectrolyte additions of approximately 5 to 2-0 lb of polyelectrolyte per ton of dry solids.

Ultimate Disposal. The ultimate disposal of oily sludges can be by barging to sea, landfill, land farming, and incineration with landfill of the ash. However, sea disposal is viewed as a short-term alternative and is eliminated as an option. The disposal of oily sludges on soil is acceptable if it can be shown that such disposal will not contaminate groundwater or contaminate storm runoff, and will not create a potential seepage problem. A proper land farming operation using soil bacteria for degradation of oils would satisfy the above requirements. The utilization of a lined landfill with leachate treatment would also meet these requirements.

Land farming of oily sludges has been successfully practiced by refineries where sufficient land area is available for proper decompositon of the oil-containing solids. Land farming involved spreading the sludge in 4 to 6-in. layers, allowing the sludge to dry about one week, adding nutrients, and then discing the sludge into the soil. Decomposition rates have found to average approximately 0.5 lb/mo-cu ft wihtout nutrient addition and 1.0 lb/mo-cu ft with nutrient addition.

Incineration of oily sludges with landfilling of the ash may provide an acceptable means of final disposal in land limited situations. The three most common types of incinerators include fluidized bed, rotary kiln, and multiple-hearth furnaces. The fluidized bed incinerator is best suited for feeds that are partially liquid so that the incinerator can be fed by pumps and screw conveyors. The multiple-hearth incinerator will be more economical if most of the feed is in the form of cake or non-pumpable solids.

Biological Sludges

The sludge handling methodology used for biological sludges is similar to that described for oily sludges. However, due to the biodegradable potential of these sludges, stabilization is required prior to disposal by sea or land. The basic process sequence for biological sludge handling consists of stabilization, thickening, dewatering, and final disposal. Often the thickening step will precede stabilization in order to reduce the stabilization cost which is highly dependent on flow. A summary of the sludge handling processes and design basis is shown in Table 5.

Biological Sludge Stabilization. The most common method of stabilizing waste biological sludge in the refining industry is by aerobic digestion. Aerobic digestion is employed to stabilize the sludge and render it suitable for land disposal, although the overall sludge quantity may be somewhat reduced and the dewatering characteristics slightly improved. Approximately 10 to 20 days detention time are required on an annual average to achieve 50 to 60 percent reduction of the volatile content of the sludge. This reduction represents about 80 to 90 percent reduction of the degradable content and is considered suitable for land application.

Thickening of Biological Sludges. The three most common processes used to thicken biological sludges in the refining industry are flotation, gravity thickening, and centrifugation. The belt pressure filter is receiving increasing attention as a thickener and dewatering device for refinery sludges.

Results of tests using refinery sludges indicate that these sludges are quite suitable for flotation thickening. Data indicate that the optimum pressure is approximately 50 to 55 psig and no polymer addition is justified. The optimum air-to-solids ratio appears to be about 0.01 lb air/lb solids and that float solids on the order of 3 to 5 percent can be readily achieved.

With gravity thickening (the most common thickening process in refinery practice), loading rates in the range of 2 to 15 lb per sq/ft per day are employed with solids concentration being achieved in the range of 2 to 4 percent solids by weight. Gravity thickeners do not require much operator attention and will perform fairly consistently provided the influent hydraulic flow when solids loading do not vary substantially. In extremely warm climates, gravity thickeners may generate obnoxious biological odors if they precede the stabilization process.

Centrifugation has been utilized sparingly for thickening waste biological sludges in the refining industry. Basket centrifuges are capable of thickening waste activated sludge to levels of 5 to 6 percent concentration with an 80 to 95 percent solids capture. One refinery has reported using basket centrifuges for thickening to a concentration of 8 percent. However, excessive maintenance was experienced because of vibrational problems.

Dewatering of Biological Sludges. The most common methods of dewatering biological sludges are vacuum filtration, centrifugation, and pressure filtration with the belt filtration press achieving an increasing use in the refining industry.

Vacuum filtration is the most common method used to dewater refinery wastewater sludges. Chemicals are usually required and the results of several tests on refinery wastewaters indicate that ferric chloride or a combination of lime and ferric chloride usually provides the optimum coagulant combination from an economical and performance standpoint. The optimum ferric chloride dosage usually ranges from 200 to 400 lb/ton of dry solids. Tests and full scale experiences indicate that vacuum filtration of refinery biological sludges will usually achieve solids concentration in the range of 10 to 16 percent at filter loading rates ranging from 1 to 5 lb/sq ft-hr. Digested sludge will usually dewater slightly better than raw, undigested sludge.

Basket centrifuges have been found to provide the best centrifugal method of concentrating waste biological solids, and there are a number of applications utilizing basket centrifuges in the refining industry. Normally, centrifuges provide a cake solids ranging from 8 to 18 percent concentration. There have been some problems in the utilization of the basket centrifuge due to mechanical vibrations; however, these problems are being solved by constructing the baskets so that it is driven from the top rather than the bottom.

Pressure filtration will usually achieve a solids concentration up to 50 percent with biological sludges, thus producing the driest cake for disposal. The pressure levels for the pressure filtration system range from 50 to 225 psig. Normally, it has been found that the pressure filtration system required higher chemical dosages than the vacuum filtration or centrifugation systems.

The use of various pressure belt filters for dewatering of waste biological solids and some oily sludges is becoming increasingly widespread in refining and other industries. A summary of data which has recently been obtained using these devices is shown in Table 6. Generally, pressure belt filters are capable of dewatering refinery waste activated sludges to keep concentrations between 15 to 20 percent. More limited data processing a combination of waste activated and oily sludges indicates cake solids contents of approximately 27 percent are obtainable. The wide range of polymer dosages used in these tests are indicative of variation both in the types of polymers and sludges processed. Loading rates to the belt presses range from 1 to 5 lb/inch belt width for biological and oily sludges. Figure 5 presents capital costs estimates for pressure belt filters as a function of the quantity of biological sludge. It is important to note from data in Figure 5 that increasing the solids content applied to the belt filter by a factor of 2 will reduce the capital cost almost in half. Consequently, it appears that thickening ahead of the pressure belt filters is definitely justified.

Ultimate Disposal. The alternative for ultimate disposal of biological sludges are similar to those for a waste oily sludge. In many cases, a thick sludge or activated sludge can be placed in 4 to 8 inch layers and utilized as a limited nutrient and soil conditioner. In this case, additional waste is removed by natural evaporation and infiltration into the underlying soil. Following initial periods of drying, the sludge layer can be disced to encourage the activity of aerobic soil bacteria.

ECONOMIC CONSIDERATIONS

It is extremely difficult to collect representative and comparable cost data on sludge handling systems in the refining industry. Different combinations of oily and biological sludges, different labor costs, and construction and capital costs which might be a function of total equipment purchased from a manufacturer (such as a complete wastewater system in which the sludge handling were only a fraction of the total equipment purchased), make it extremely difficult to develop cost as a function of size of equipment. Therefore, some data are gathered which are considered to be reliable and presented in a form for discussion in this section.

In Figure 6, a sludge handling system is shown whereby biological and oil sludges were combined for dewatering by pressure filtraton or vacuum filtration prior to landfill (5). The biological solids (1,070 tn/yr) were aerobically digested and gravity thickened. The oily sludges (1,000 tn/yr) were thickened and stored. The combined biological and oily sludges (2,070 tn/yr) were dewatered by pressure (Alt. I) or vacuum filtration (Alt. II) and transported to landfill. The third alternative consisted of direct transport by piping of the combined thickened biological and oily sludges for land farming.

Costs for Alternative I (dewatering using pressure filtration followed by landfill disposal of the sludge cake) were based on operation of the pressure filter 140 hr/wk and transport of the dewatered cake approximately two miles to the landfill site. Costs were included for the use of 1 lb conditioner/lb sludge dewatered and it was assumed that a cake having a solids content somewhat greater than 50 percent would be obtained. The filters had facilities included for precoating and were designed for a two-hour cycle time. The total sludge volume transported to the landfill site was 18 cu yd/day.

Costs for Alternative II employing vacuum filtration for sludge dewatering included operation of the vacuum filter 135 hr/wk. The filter was designed using a loading rate of 1.4 lb/sq ft-hr and it was assumed that a 40 percent cake would be produced. The vacuum filter was also designed as a precoat system and it was assumed that the amount of precoat required would equal 10 percent of the weight of sludge to be dewatered. Transport distance to the landfill was also assumed to be 2 mi and the quantity of cake requiring disposal was calculated to be approximately 40 cu yd/day.

Costs for land farming of the sludge (Alternative III) were based on the application of sludge in 4 to 6 inch layers at an application rate of 5 lb/sq ft-yr. It was assumed that following application the sludge would be allowed to dry for one week during which nutrients would be added to the soil, and subsequently followed by discing of the sludge into the soil.

In this situation, dewatering by vacuum filtration was 15 percent cheaper than pressure filtration; however, the transportation costs were almost twice as much due to the wetter vacuum filter sludge. In summary, the vacuum filtration scheme was approximately 4 percent cheaper than the pressure filtration scheme. However, Alternative III, land farming, was about 50 percent more economical than either pressure or vacuum filtration. The land farming assumes discing with a tractor and disc rather than the more expensive bulldozer used in some other published methods.

Pressure Filtration Costs

Estimated costs for pressure filtration dewatering of oily sludges is presented in Table 7. These costs were based on dewatering API separator bottoms, tank bottoms, decant pit sludges, flotation units solids, spent clays, oil emulsions, and other miscellaneous oily sludges (6). Each press was designed using a 1.5-inch cake thickness, and 64-inch diameter plates. It was also assumed that the feed sludges would be heated to a temperature of 150° to 200°F prior to the dewatering period. It was assumed that lime would be used as a conditioning agent with a dose of 0.1 lb lime/lb dry solids dewatered.

Dewatering costs presented in Table 7 range between $26 and $40/tn including both capital and operating costs. Costs for pressure filtration shown in Figure 6 are substantially higher than those shown in Table 7 where an in-depth cost analysis of pressure filtration was performed. The higher costs associated with pressure filtration in Figure 6 are partially attributable to the presence of biological solids which make the sludges more difficult to dewater and require larger quantities of conditioning chemical. In addition, a substantially larger quantity of sludge was used as a basis of the estimates presented in Table 7 - 9,200 tn/yr compared to 2,070 tn/yr used in Figure 6.

The analysis presented in Table 7 indicates that dewatering costs are minimized with three shifts per day operations and become progressively higher with 2 and 1 shift per day operations. However, the cost estimates for three shifts per day operation contain no flexibility in the design since only one machine was used for 24 hr/day operation. It was estimated that the use of two presses, each having the capacity to dewater 60 percent of the total solids throughout, would add approximately $125,000/yr to the total annual cost. On a unit cost basis, this would increase the total sludge dewatering costs to approximately $39/tn. In many instances, it might be more economical to provide storage facilities for holding sludge when maintenance of the press is required. In individual cases, the optimum design would require consideration not only of initial construction and operating costs but also of labor policies which might interfere with three shift per day operation, the operational flexibility desired, the degree to which alternative designs could accommodate plant expansion in the future, etc.

Costs for Centrifugation of Oily Sludges

In Table 8, the cost of a centrifuge system for handling oily sludges is presented. The cost to dewater 660 tn/yr of flotation unit skimmings using a basket centrifuge was estimated to cost $160/tn (7). A two-stage system consisting of a horizontal solid bowl and disc-nozzle centrifuge in series for handling combined oily sludges was estimated to cost only $45/tn for treating 1,750 tn/yr. Costs for the basket centrifuge treating flotation skimmings was estimated based on a 17 gpm flow rate, 90 percent on-stream factor, and 2 percent influent solids concentration. Costs of the basket centrifuge and disc-nozzle system in series was estimated based on a 7 percent influent solids concentration at a flow of 13 gpm and a 90 percent on-stream factor. In using the horizontal solid bowl and disc-nozzle centrifuge in series, the feed would initially be processed through the basket centrifuge with the centrate and the emulsion contained in this stream being broken and handled with the disc-nozzle centrifuge.

Incineration Costs

Costs for the incineration of refinery sludges using alternative dewatering methods is presented in Table 9. In each case, the sludge consisted of flotation unit solids, refinery oil sludges, spent clays and emulsions (whitewater). Each example was based on dewatering 8,400 tn/yr dry solids. If only the flotation solids are dewatered using centrifugation and the remainder of the streams are fed to the incinerator without dewatering, the total cost of incineration would amount to approximately $53/tn. By dewatering both flotation solids and oily sludges using centrifugation, costs were observed to decrease approximately $45/tn. Pressure filtration of all wastestreams prior to incineration further reduced the total incineration costs to approximately $41/tn.

Land Farming

For Allowable oil loadings ranging from 2.5 to 25 lb/sq ft-yr, the required land area for land farming of oily sludges can be determined from Figure 7. Literature costs for land farming of oily sludges are shown in Table 10. Although the total costs per ton of waste are approximately the same, $22 and $24/tn, there is a significant discrepancy in each case regarding the loading rate of oil to the soil, cost of transportation, and cost of cultivation. The cost for land farming taken from Figure 6 totaled $35/tn of solids. Based on a reported 50 percent oil content for this sludge, the cost would be equivalent to approximately $70 of oil applied to the land. Costs for this latter example were developed based on an application rate of 5 lb oil/cu ft-yr applied to a depth of approximately 6 in. which is equivalent to a surface loading of approximately 2.5 lb/sq ft-yr. While the unit costs for land farming estimated in each of these three examples are not extremely divergent, very significant differences exist for cost estimates for individual items. It is felt that this is partially the result of differences inherent to each individual situation. However, it is also likely more accurate costs will be available as the practice of land farming continues to be used in the refining industry.

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BIOGRAPHIES

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TABLE 1. REFINING INDUSTRY SLUDGE DISPOSAL PRACTICES[a]

METHOD	DISTRIBUTION (%) 1973	 1983 (est.)
LANDFILL	50	44
LAGOONING	40	19
LAND FARMING	9	34
INCINERATION	1	3
ONSITE DISPOSAL	44	73
OFFSITE DISPOSAL	56	27

[a] Jacobs Engineering Company. "Assessment of Hazardous Waste Practices in the Petroleum Refining Industry." Environmental Protection Agency, Contract Number 68-01-2288, Pasadena, California, June 1976.

TABLE 2. CHARACTERISTICS OF REFINERY SOLIDS WASTES (Ref. 3)

Waste Type	Typical Composition, Percent Oil or Hydrocarbon	 Water	 Volatile Solids	 Inert Solids	Characteristics
API Separator Sludge	15	66	6	13	Fluid slurry of oil, water and sand
Tank Bottoms	48	40	4	8	Oil-water mixture
Chemical Treatment Sludge	5	90		5	Slightly viscous fluid
Air Flotation Froth	22	75		3	Thick, oily fluid
Precoat Vacuum Filter Sludges	22	29		49	Temperatures
Biological Treatment Sludges					
Raw	0	98	1.5	0.5	Water Consistency
Mechanically Thickened	0	94	4	2	Thick, but pumpable
Centrifuged	0	85	10	5	Viscous-peanut butter consistency
Vacuum Filtered	0	75	15	10	Wet crumbly solid
Screw Pressed	0	40	40		Intact, solid cake
Water Treatment Sludge	0	95		5	Pumpable Fluid, sometimes gelatinous

Cross, F. L. and J. R. Lawson. "A New Petroleum Refinery." American Institute of Chemical Engineering Symposium Series, Vol. 70, No. 136, P. 812.

TABLE 3. ESTIMATES OF REFINERY SOLID WASTE QUANTITIES (Ref. 3)

Waste Types	Unit Loads
API Separator Sludge	200 mg/l Suspended Solids
Chemical Treatment (API Separator Effluent)	50 mg/l Suspended Solids Removed Only
Biological Sludges	0.7 lb Dry Solids per lb BOD Removed
Water Treatment Sludge	
A. Lime Soda Ash	2 parts Dry Sludge per 1 part Hardness Removed
B. Ion Exchange	0.4 lb Salt per 1,000 Grains Hardness
Office Wastes	1.0 cu yd per Employee per Month
Cafeteria	0.6 lb per Meal

Cross, F. L. and J. R. Lawson, "A New Petroleum Refinery." American Institute of Chemical Engineering Symposium Series, Vol. 70, No. 136, p. 812

TABLE 4. SUMMARY FOR THE THICKENING AND DEWATERING ALTERNATIVE OF OILY SLUDGES

Type of Sludge	Process	Average Performance	Design Parameters	Comments
Oily Sludge	Thickening			
	Gravity	3-7 percent solids, 50% recovery	5-30 lb/sq ft-day	Low solids and oil recovery
	Flotation	84-93% solids recovery, 3.5 - 5.5% float solids	Untreated sludge 420 - 2,000 mg/l TSS, 100% recycle, 50 psig saturation pressure	Successful for froth flotation sludges but impractical for other oily sludges
	Dewatering			
	Centrifugation	75-90% solids recovery when charged with heated oily sludges. Oily phase will consist of 1-5% solids and cake will contain 50-60% solids. Nozzle ejector centrifuge separates 95-98% of oil in oily phase and 205% in the nozzle and nozzle water. 30-50% of nozzle ejector feed solids will be removed with oily phase.	Flow rate 50-350 gal/hr	A vertical solid bowl type is not recommended for dewatering most oily sludges
	Vacuum Filtration		Avg. Filter Rates gal/hr-sq ft slop-oil emulsion - 1.7 separator sediment - 2.8 flocculation sludge - 8.6 acid oil - 2.4 Filter Time Required, percent, slop-oil emulsion - 37.8 separator sediment - 20.1 flocculation sludge - 10.7, acid oil - 7.8, precoating - 8.5, downtime - 15.1	To dewater oily sludges, a precoat vacuum filter should be used and solids should be heated above 170° F. Solids should be suitable for landfill following vacuum filtration. Increased temperature for feed improves performance. Addition of spent clays decreases oil recovery and solids F.H. rate
	Pressure	5-20% oil, 40-70% solids cake	2-hr cycle time, feed contents 12-38.5% TSS, 6-23% oil. Temperature of feed 58-180° F	Heating of feed required for satisfactory filtration. Lime or spent caustic added.

TABLE 5. SUMMARY OF BIOLOGICAL SLUDGES

Type of Sludge	Process	Average Performance	Design Parameter	Comments
Biological Sludges				Similar to oily sludges but should be stabilized due to putrescible nature
	Thickening Gravity	2-4% solids concentration by weight	Loading rate 2-15 lb/sq ft-day	If surface loading rate is excessive poor solids recovery will result
	Centrifugation	5-6% with basket centrifuges, 80-95% solids capture	Feed rate 5-200 gpm	There is little information available
	Flotation	Cake solids 2.6 - 4.0%	50-60 psi, 100-500% recycle Solids loading 216 sq ft-hr hydraulic loading 1-4 gpm/sq ft	Sludges quite amenable to flotation thickening
	Dewatering Vacuum Filtration	Solids concentration 10-16%	Loading rate 1-5 lb/sq ft-hr	Chemical usually required to decrease specific resistance. $FeCl_3$ or lime and $FeCl_3$ usually. Optimum $FeCl_3$, 200-400 lb/ton of solids
	Centrifugation	8-18% cake solids. Solids recovery 20-90%	Feed rate 4-90 gpm	Basket type found to be best. There have been problems due to mechanical vibrations in the centrifuge.
	Pressure Filtration	50% solids	Pressure levels 50-255 psig	Normally requires higher chemical dosages than for vacuum filters or centrifuges.

TABLE 6. PILOT SCALE PERFORMANCE DATA OF PRESSURE BELT FILTERS

Plant No.	Type of Sludge	Belt Width (inches)	Solids(%) Feed	Solids(%) Cake	Polymer Dosage lb/ton	Polymer Dosage $/ton	Throughput lb/hr	Throughput gpm/in. belt width
1	Fresh Waste Activated - Refinery	20	0.7	17	--	--	20	0.25
2	Fresh Waste Activated - Refinery	20	2	20	2	--	150	0.75
3	Fresh Waste Activated - Refinery	20	1.5	15	25	55	70	0.45
	Aerobically Digested Waste Activated - Refinery	20	3.1	17	150	18	230	0.75
	API Separator Bottoms	20	4.6	23	8	1.06	275	0.60
4	Fresh Waste Activated + Oil Tank Bottoms + API Separator Bottoms	20	8	27[a]	3	4.20	320	0.4
5	Fresh Waste Activated – Pulp and Paper Industry		1-5	12-20	10-20	15-40	--	--

[a] Cake Contained 50% Oil

TABLE 7. VARIATION OF PRESSURE FILTRATION COST WITH OPERATING CONDITIONS

On-Line Time (hr/wk)	56	112	168
Influent Characteristics			
Total Solids (tn/yr)	9,200	9,200	9,200
Oil (tn/yr)	8,000	8,000	8,000
Cycle Time (hr)	2.5	2.5	2.5
Cake			
Solids (% wt)	55	55	55
Oil (% wt)	5	5	5
Design Information			
Machines	2	1	1
No. Plates	80	80	55
Capital Cost ($)	1,970,000	1,200,000	1,060,000
Operating Cost ($/yr)	80,000	73,00	91,000
Annual Cost ($/tn)	368,000	246,000	241,000
Unit Cost ($/tn)	40	27	26

Note: Costs in 1977 $

TABLE 8. COST OF CENTRIFUGATION FOR OILY SLUDGE HANDLING

	Basket	Solid Bowl and Disc-Nozzle
Type Sludge	Flotation Skimmings	Oily Sludges
Total Solids (tn/yr)	660	1,750
Operating Time (hr/wk)	168	168
Capital Cost ($)	260,000	360,000
Operating Cost ($/yr)	64,000	18,000
Annual Cost ($/yr)	106,000	78,000
Unit Cost ($/tn)	160	45

Note: Costs in 1977 $

TABLE 9. COST OF INCINERATION FOR OILY SLUDGES[a,b]

Incineration Cost	Dewatering Method Flotation Solids By Centrifugation[c]	Flotation Solids and Oily Sludges by Centrifugation[c]	Pressure Filtration[d]
Capital ($)	1,110,000	919,000	767,000
Operating ($/yr)	265,000	229,000	222,000
Annual ($/yr)	443,000	378,000	345,000
Unit Cost ($/tn)	53	45	41

[a] Treated Sludge consisted of flotation unit solids, refinery oily sludges, spent clays, and white water. Example for 8400 tn dry solids/yr.

[b] Costs are 1977 \$. Costs include \$6.30/yd^3 for ash disposal. No dewatering cost included.

[c] Other solids not dewatered prior to incineration.

[d] All solids dewatered prior to incineration.

TABLE 10. ECONOMICS OF LAND SPREADING OF OILY SLUDGES

	Kincannon (7)	Huddleston Cresswell (8)
Soil Loading (lb oil/ft^2 - yr)	12	1.5
Oil Fraction of Sludge (%)	33	25
Transport	2.30/tn	4.80/tn
Land		3.90
Site Preparation		5.95
Fertilizer	1.20	1.25
Cultivation	18.85	1.75
Analytical Support	--	6.60
	$22.35/tn Waste $67.05/tn Oil	$24/tn Waste $97/tn Oil

Note: Costs are 1977 $

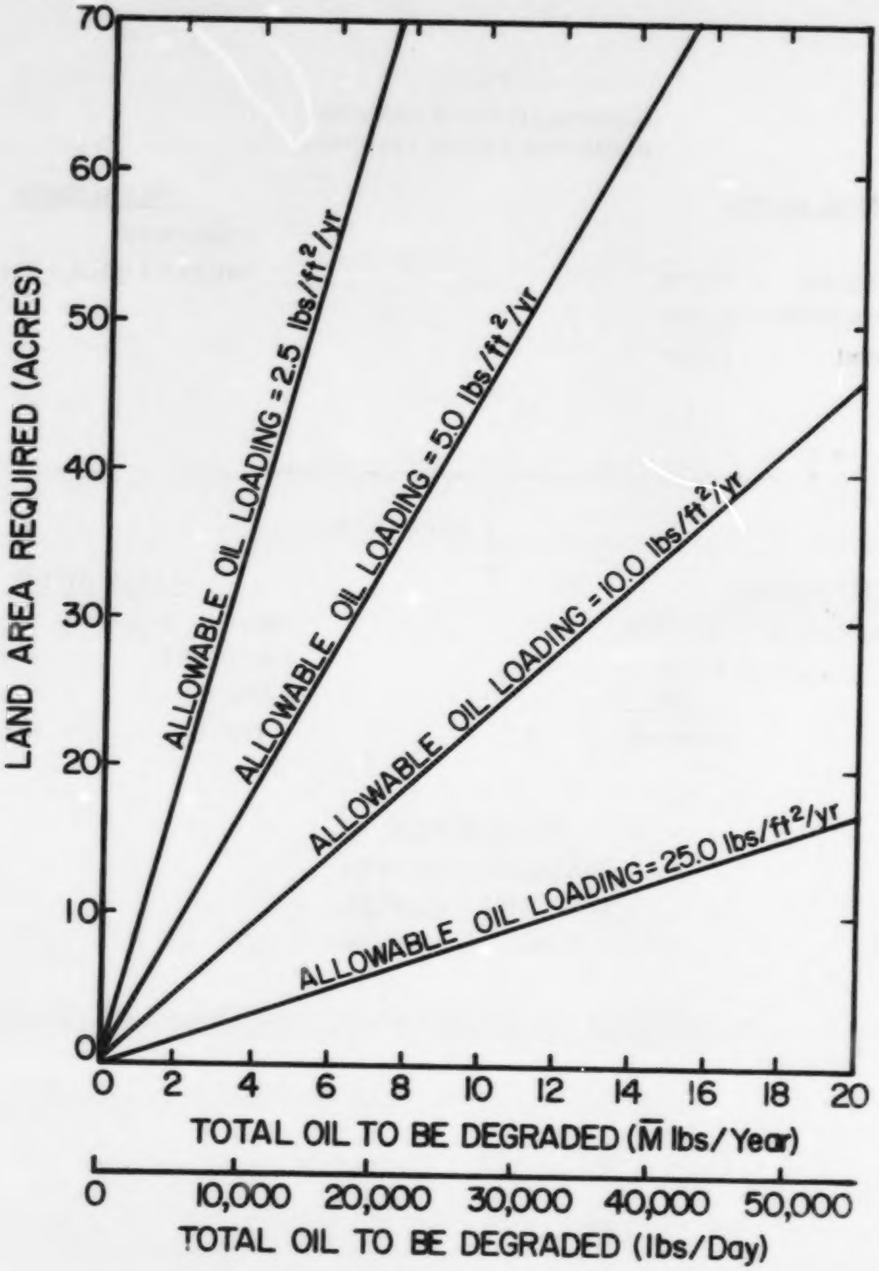


FIG. 7. AREAS REQUIRED FOR SURFACE BIO-OXIDATION OF OIL AS FUNCTION OF ALLOWABLE OIL LOADING

FIG. 6

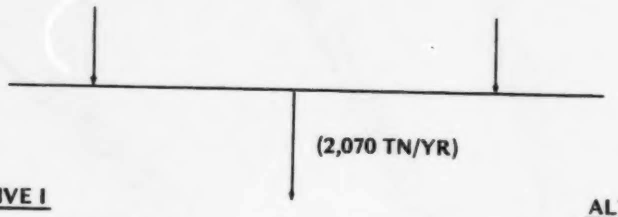
ALTERNATIVES FOR HANDLING BIOLOGICAL AND OILY SLUDGES

BIOLOGICAL SOLIDS

(1,070 TN/YR)
AEROBIC DIGESTION = \$53/TN
GRAVITY THICKENING = \$22/TN
SUBTOTAL \$75/TN

OILY SLUDGES

(1,000 TN/YR)
THICKEN & HOLD = \$38.50/TN



ALTERNATIVE I

PRESSURE FILTRATION = \$69.70/TN
TRANSPORT = \$ 8.50
LANDFILL = \$ .70
TOTAL = \$78.90/TN

ALTERNATIVE II

VACUUM FILTRATION = \$59.20/TN
TRANSPORT = \$16.00
LANDFILL = \$ .70
TOTAL = \$75.90/TN

ALTERNATIVE III

TRANSPORT = \$32.70/TN
LAND FARM = \$ 2.60/TN
TOTAL = \$35.30/TN

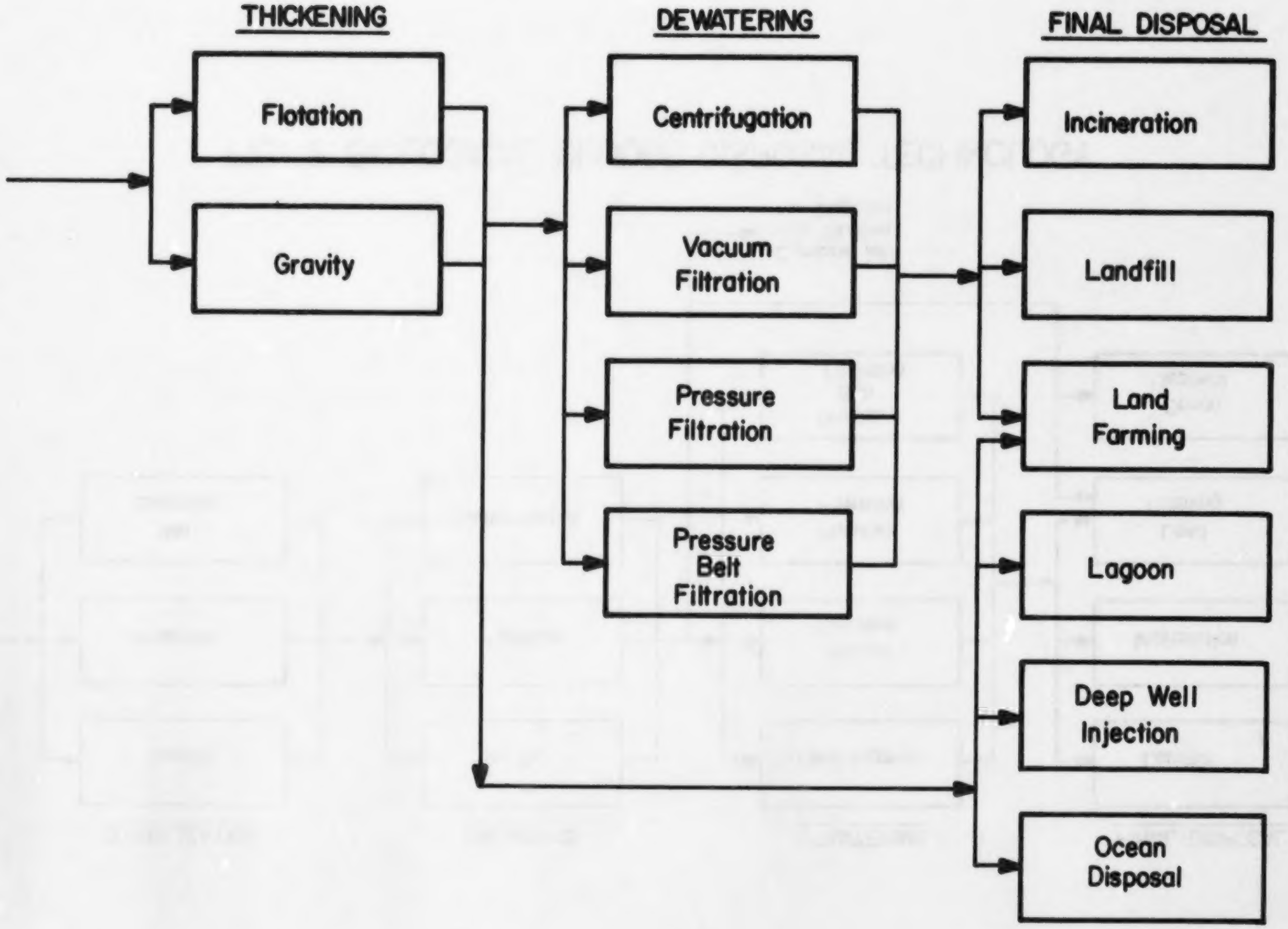


FIG. I. OILY SLUDGE DISPOSAL TECHNOLOGY

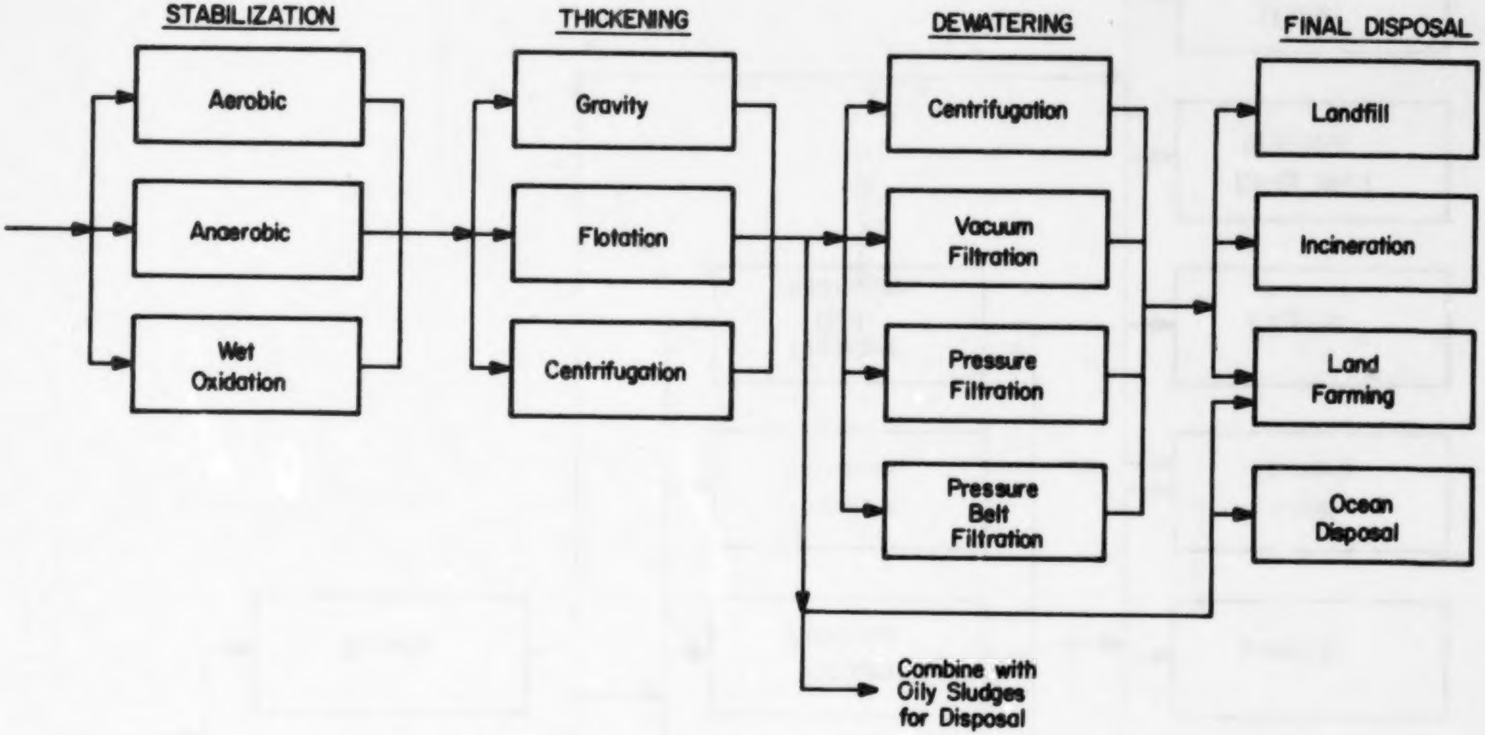


FIG. 2. BIOLOGICAL SLUDGE DISPOSAL TECHNOLOGY

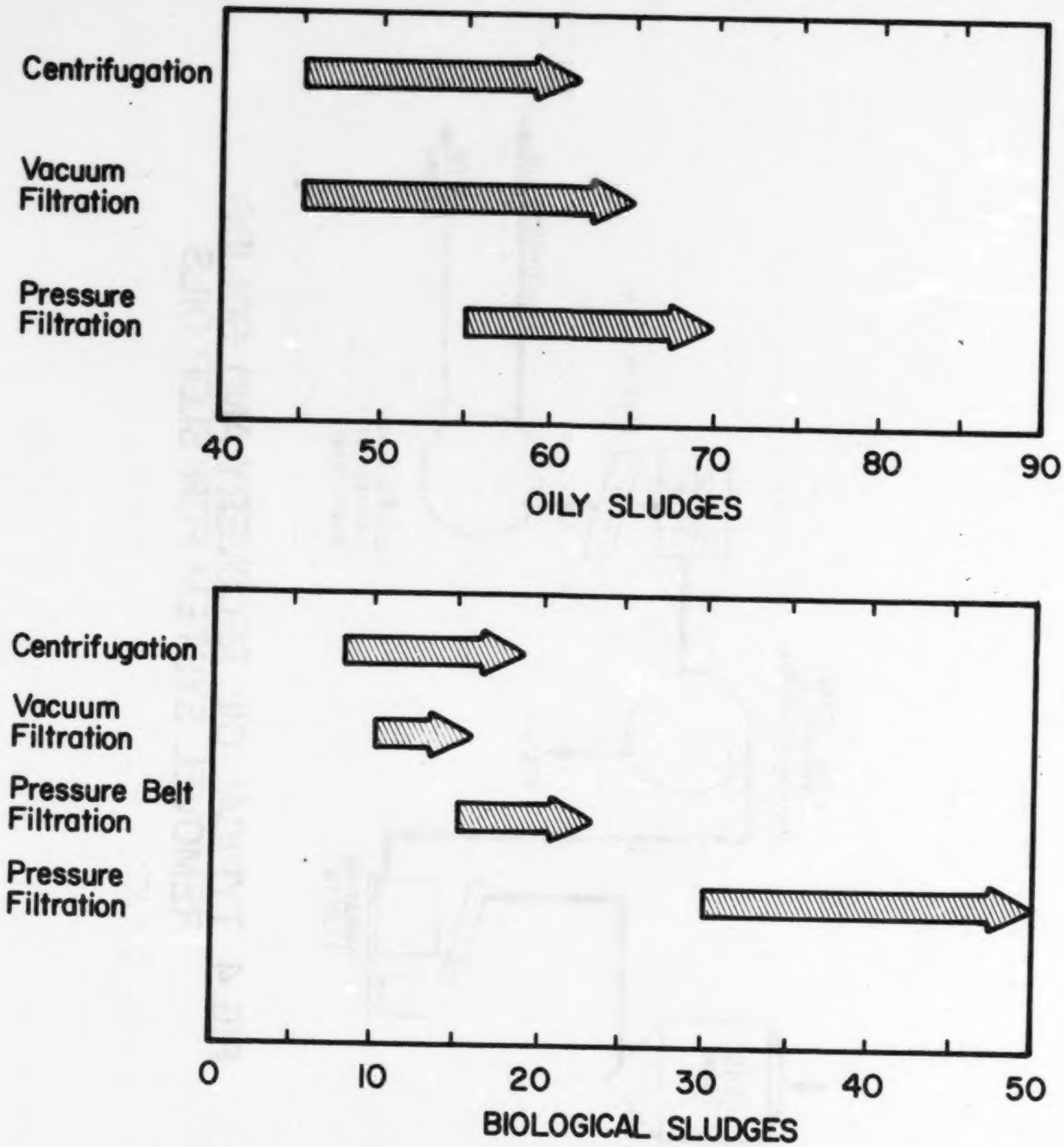


FIG.3. SOLIDS CONCENTRATIONS OBTAINABLE USING VARIOUS SLUDGE DEWATERING PROCESSES

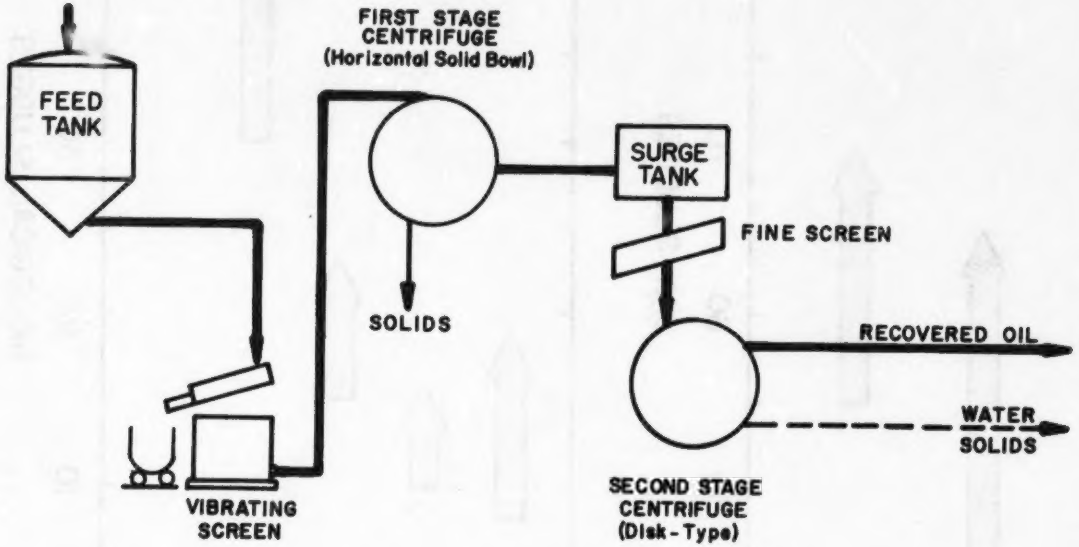

FEED TANK
FIRST STAGE CENTRIFUGE (Horizontal Solid Bowl)
SURGE TANK
FINE SCREEN
SOLIDS
RECOVERED OIL
WATER
SOLIDS
VIBRATING SCREEN
SECOND STAGE CENTRIFUGE (Disk-Type)

FIG. 4. TYPICAL OIL RECOVERY AND SOLIDS REMOVEL SYSTEM FOR SLOP OILS

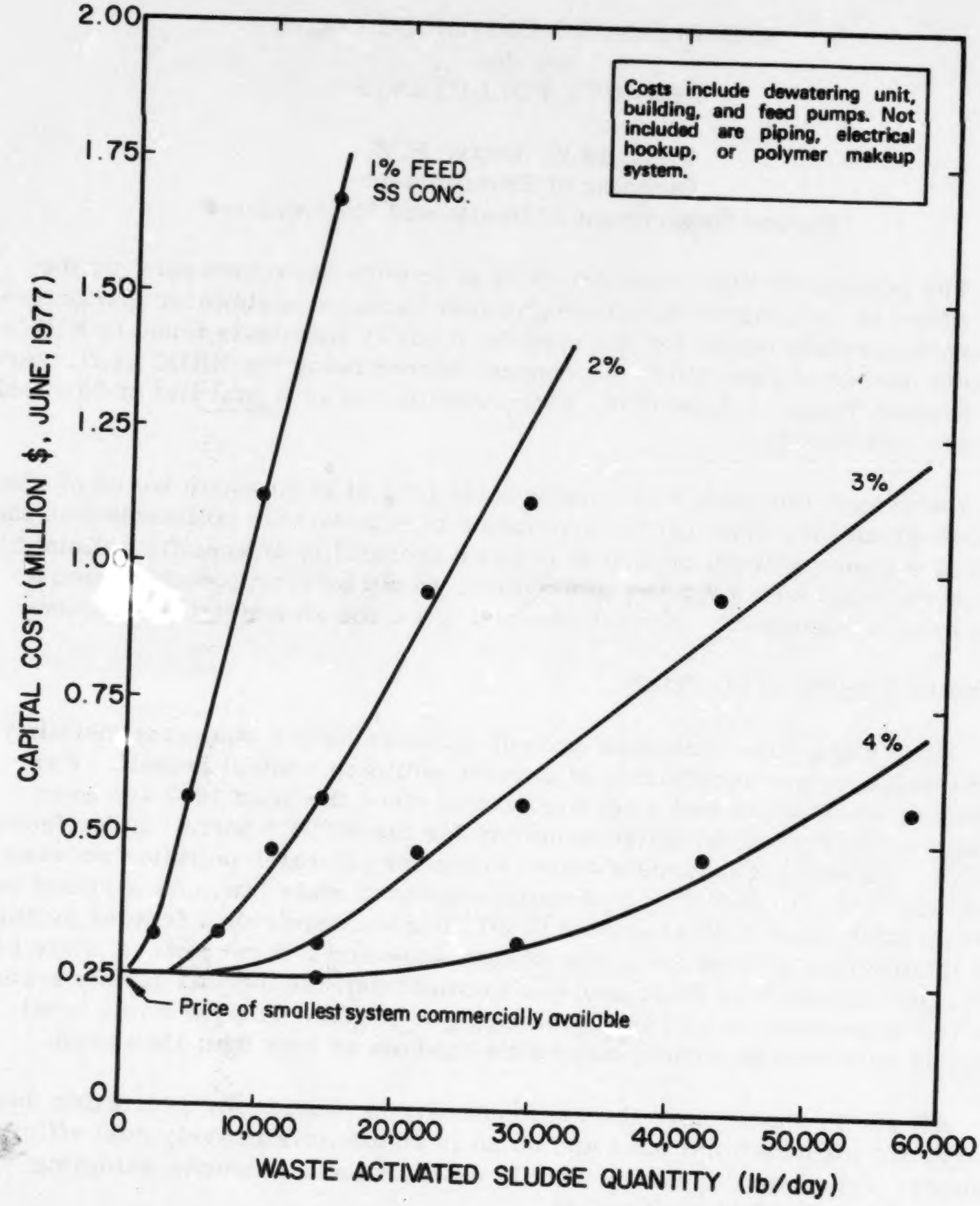


FIG. 5. CAPITAL COST FOR PRESSURE BELT FILTER SYSTEMS FOR DEWATERING WASTE ACTIVATED SLUDGE

COMPLIANCE MONITORING COSTS
for the
PRIORITY POLLUTANTS

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The purpose of this presentation is to provide state viewpoint on the cost effect in compliance monitoring of point source wastewater discharges if permits contain limits for the specific priority pollutants found in EPA's consent decree of June 1976: the consent decree being the NRDC et al. versus Russell Train, 8 June 1976, which resulted in an initial list of 65 specific toxic pollutants.

I approach this task with considerable lack of enthusiasm based on the preconceived idea that such incorporation of monitorable pollutants into the permit system, without regard to need or probability of specific pollutant occurrence and as a routine requirement, would be irresponsible from a cost benefit standpoint. Nevertheless, I offer you an analysis as follows:

PERMIT RESPONSIBILITIES

Many state water pollution control agencies have a dual responsibility in the issuance and monitoring of a water pollution control permit. For example, Kansas has had a permit system since the year 1907 and even though we have been delegated authority for the NPDES permit under federal law, we still must issue a state permit for all water pollution sources incorporating all conditions and requirements of state law. As a result we issue a joint state-federal permit to all sources requiring a federal permit and incorporate all requirements of both state and federal law. A state permit alone is issued to those sources exempt from the federal permit system such as non-overflowing (non-discharging to surface waters) waste treatment or retention facilities, and cattle feedlots of less than 1000 head.

All states should have the responsibility to provide for protecting their waters for all beneficial uses and do so in an administratively cost efficient manner. Irrelevant or unnecessarily extensive and exhautive sampling programs can seldom be justified.

ENVIRONMENTAL LABORATORY FUNCTIONS

For the past 70 years the laboratory for the Division of Environment has been required by statute to be a "fee-supported" laboratory from the standpoint of analytical workload received from other than department staff.

As such, routine cost determinations are made based on total analytical workload, administrative costs, rent, personnel costs, fringe benefits, and equipment amortization. For example, the gas chromatograph-mass spectrometer which is pertinent to the problem at hand and which was acquired at a cost of $150,000, has been amortized over a period of seven years.

It is a policy of our department to not compete with private laboratories and we do not accept outside work except on an emergency or temporary basis. Monetary charges are made on our cost factors and from a practical standpoint a profit factor is not involved. The analytical costs are established through administrative rules and regulations.

Our laboratory has highly qualified professionals even though it is geared to "mass production techniques" due to workloads. Last year's analytical workload was as follows:

Central Laboratory Samples

47,153	bacteriological
2,150	partial chems
2,350	complete chems
450	organic chems

Field Laboratory Samples

2,787	complete chems
1,963	dissolved oxygen
2,683	nutrients
488	heavy metals
908	pesticides
384	radiological
2,852	bacteriological
313	biological

It is projected that the above workload will increase significantly next year and in subsequent years particularly in relation to organics. The significant factor being that as a state agency we do have benefits of volumetric cost savings.

REFINERY POINT SOURCE PERMITS

Kansas has 11 principal petroleum refineries with a crude oil capacity of approximately one-half million barrels per day. These refineries have long been accustomed to regulation and permits under Kansas law with perhaps the single most significant requirement occurring in the mid-1950's in providing for total retention of water falling on refinery property that would occur during a 5-inch rainfall. This is approximately equivalent to the maximum probable 24-hour rainfall occurring once in 10 years.

The state-federal wastewater permits presently in effect in Kansas require monitoring for and place limits on 12 potential pollutants listed as follows:

BOD
TSS
COD and/or TOC
Oil and Grease
Phenolic compounds
Ammonia
Sulfide
Total chromium
Hexavalent chromium
pH
Sulfates
Chlorides

Compliance monitoring - inspection and sampling - involves the following cost considerations:

Engineer evaluation - two man-days Includes salary, transportation costs including delivery of samples to lab., and report writing	$175.00
Lab costs (assuming two samples)	67.50
Clerical support	6.00
Follow-up contingencies (discussions, minor corrections)	50.00
	$298.50

For the same compliance monitoring inspection but with the 65 priority pollutants made a part of the permit, the above base costs of $298.50 would remain constant but an additional $287.60 lab cost for each of the two samples will be involved giving a total state cost of $873.70 for each inspection. Each additional sampling point incurs a base lab cost of $325.35 which includes the 65 priority pollutants as opposed to a base lab cost of $67.50 for analysis of pollutants in existing permits.

For this example monitoring inspection, inclusion of the 65 priority pollutants increases laboratory costs by a factor of nine and total costs by a factor of three.

One might rationalize that inclusion of the 65 priority pollutants is justifiable in the case of petroleum refinery permits and that two inspections per year with four samples at a state cost of ± $1750 is nominal. However, the inclusion of the priority pollutants in all permits within the state would result in a program point source monitoring cost in excess of

$500,000 if only one appraisal and sample per year was provided. In comparison, this $500,000 cost exceeds the total Section 106 program grant to Kansas by $100,000.

The total impact of incorporating the 65 priority pollutants into point source permits cannot really be appreciated without additionally considering routine monitoring and reporting of all pollutants by industry as well as municipalities under the recently announced pretreatment requirements for wastes discharged to municipal systems. Fortunately, these issues are outside the scope of this presentation as well as beyond the capabilities of my TI-SR 51 hand calculator. It should be stated that the pretreatment standards proposal in Kansas is estimated to cost $500,000 if the state administers the program and $250,000 if five or six municipalities having approximately 60% of the significant sources within their systems administer the program. These cost estimates do not consider monitoring costs of industry nor do they include analysis for the 65 priority pollutants except on a problem-need basis.

Finally it must be recognized that industry generates large volumes of solid and liquid hazardous wastes that are normally controlled through solid waste laws. In relation to "petroleum refining and related industries" a recent survey of 31 such industries in Kansas revealed that 2-1/2 million gallons and 3,743 tons of potentially hazardous and toxic liquid and solid wastes are generated annually. These wastes are not normally discharged to surface waters but are handled through solid waste outlets and facilities. These wastes are principally caustics, acids, and catalytic materials and are being handled at a state administrative cost estimated at $1500-$2000 per refinery per year. The total "solid wastes" of the state in many instances contain many of the 65 priority pollutants but for now are considered outside the scope of jurisdiction.

SUMMARY

1. The 65 priority pollutants should be incorporated in point source permits on a specific problem-need basis.

2. As a minimum, Kansas as a state will most likely incorporate monitoring for the 65 priority pollutants at select sites within the existing surface water monitoring network to determine if there are any potential problem stream segments.

3. Consideration should be given to analysis for the 65 priority pollutants from select point source dischargers, on a random basis, or during intensive river basin surveys.

4. In our opinion, cost-benefit factors do not warrant overall inclusion of the 65 priority pollutants in all point source permits as monitorable pollutants.

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"ANALYTICAL COSTS AND THE PROBLEM POLLUTANTS"

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ABSTRACT

Recent studies of the EPA into the water supplies of 80 cities indicated a predominance of six volatile halogenated organic compounds and the presence of many other trace organic compounds. As the result of a court agreement between the National Resources Defense Council and the EPA in June of 1976, a survey of the chemical and affiliated industries was initiated by the EPA. This survey is underway and, as presently constituted by the EPA, will focus on 109 specific organic compounds, 13 metals, cyanides, phenols and asbestos.(1)

Analytical costs are usually minimal in the overall cost of any process or treating facility. If the purchase of a GC/MS system is required ($140,000), capital costs of up to $200,000 can be incurred in the analysis of these pollutants. Recently publicized figures have indicated cost factors as low as $2,000 per sample by contract laboratories. However, the analytical methodology is as yet unproven. Total analytical costs of near $20,000 per refinery sampling visit can be expected if statistical considerations, quality assurance and a refinement of the analytical methodology are taken into consideration for the present EPA survey.

Approximately 75 percent of the organics in water will not be covered by this survey because techniques suitable for their analysis on a broad scale have not yet been developed.(2)

Specific details of the current EPA survey will be presented and will include an analysis of capital instrument costs, sampling costs, analytical method costs, quality assurance costs and final reporting costs.

INTRODUCTION

In considering the cost of analysis of the priority pollutants, it is necessary to define the compounds that are to be analyzed and to define the procedures that are to be used in their analysis. The basis for both of these requirements is the "Sampling and Analysis Procedures for Survey of Industrial Effluents for Priority Pollutants" as released in revised form in April, 1977, by the EPA.(1) In this document, 109 specific organic compounds are identified for analysis as well as 13 metals, asbestos, cyanide, and phenolics. Our discussion of the cost of these methods is not an endorsement on our part of the methods that are specified by the EPA for this screening survey. The methods for trace organics specified in these procedures are tentative. These methods cover at most only 25 percent of the total organics in water. If we are looking then at the total cost of the analysis of trace organics in water, at present costs are minimal. It is likely that more compounds will be added to the list or that the scope of the analysis will be broadened to something quite different from that now proposed by the EPA.(2)

Various cost elements can be identified in treating the overall costs of analysis. These elements are equipment, sampling, analytical procedures, quality assurance, and reporting.

Equipment

Equipment costs arise from an assortment of analytical instruments that are needed for the priority analyses. These costs are identified and summarized in Table 1. For the 109 organic compounds, the EPA procedures specify a coupled gas chromatograph-mass spectrometer data system (GC/MS), for both qualitative and quantitative use. The cost of the GC/MS can vary considerably depending on the mass spectrometer configuration and the accompanying data system. We have obtained cost estimates that have ranged from fifty to two hundred thousand dollars. Our estimate for the equipment that is needed to do the analysis is $140,000. This $140,000 would purchase a GC/MS-computer system capable of high speed scanning with sufficient resolution and data handling capability for the determination of the trace organics.

For metals analysis an atomic absorption spectrometer equipped with a graphite furnace and automatic sampler is required. The graphite furnace allows for determination of μg/l concentrations in microliter samples. The automatic sampler is convenient when many samples need to be run for one metal. Cost of such an instrument is approximately $20,000.

A gas chromatograph with an electron capture detector is needed for the separation and determination of pesticides at the μg/l level. Such an instrument could also be used for quantitative analysis of the volatile organics on the priority pollutant list, which are less numerous than the non-volatiles and therefore more easily separated and identified. Cost of an electron capture gas chromatograph is about $10,000.

The third major instrument is not absolutely necessary for priority pollutant analysis but is helpful in obtaining an estimate of the impact of the priority pollutants on the total organic content of the sample. This is a total organic carbon analyzer, which gives a fast determination of total trace organics in water and is a mainstay of most well equipped water analysis laboratories. Most TOC analyzers cost about $10,000.

The last instrument needed is an ultraviolet-visible spectrophotometer. This is required for the cyanide and phenolics analyses. Although the UV range is not specifically required, it is useful for determining aromatic hydrocarbons, which absorb in this region. UV-visible spectrophotometers cost about $7,500.

Other items of miscellaneous equipment which are required for priority pollutant analysis include a composite sampler at $4000, a liquid sample concentrator at $3000, and an analytical balance at $2000. In addition, a flameless atomic absorption unit for mercury determination costs $1000 and a water purification system to produce ultrapure water for sample blanks costs about $2000. Finally, the assorted laboratory glassware needed is estimated at $2000.

As shown in Table 1, this leads to total equipment costs of just over $200,000. It is assumed that this equipment would be dedicated to water analysis.

Sampling

In considering sampling costs a principal consideration is the frequency of sampling. This frequency is in turn dictated by the variation in composition of the stream being sampled. Figure 1 is a plot of the average monthly TOC for one of our refineries. Four sampling visits in one year should be adequate to account for the seasonal variation evident in Figure 1. Subsequent sampling visits could take place on a less frequent schedule based on a review of the analytical data.

Short term variation of stream composition also occurs as shown in Figure 2. This figure is a plot of the daily TOC for four of the months shown in Figure 1. A 72-hour sample visit ought to be a long enough compositing period to average the daily variation evident in Figure 2. This 72 hours compositing period has been used by the EPA in their refinery survey program for industrial effluents. In addition some daily samples should be taken to assure that an upset has not resulted in an unusually high level of a particular pollutant.

Costs begin with the equipment needed for sampling which should run about $500, unless an automatic composite sampler is used, as listed previously in Table 1. For one sampling trip, travel costs, including per diem expenses at the site and local travel costs, are estimated at $1100. If two men are used to sample at four-hour intervals over a 72-hour period, it is estimated each will work a 50-hour week. At manpower costs of $40/hour this comes to $4000. Sample shipment costs are estimated at $250, making a total of almost $6000 for one sampling trip. Assuming four trips a year to allow for seasonal variation, the sampling cost for one refinery site is $24,000 per year.

Analytical Procedures

Before considering the details of the cost of the EPA analytical procedures, some discussion is warranted on the analytical methodology itself. It is our position that the complexity of the analytical procedures demands that extensive quality assurance be built into the analysis. Standard methods that are listed in the EPA procedures cover metals,(3)(4) phenols,(5) and cyanides.(3) All of these procedures have been published and have had rather wide use in the industry. While there may be problems with the accuracy and precision of some of these methods, they are at least in common use. Because of the nature of the analytical procedures for asbestos(6) there are relatively few laboratories in the country that are capable of running the analysis.

Our attention is focused on the methods for trace organics, which are not in common use and must be considered tentative. Of the 109 organic compounds, 32 are analyzed in the purgable (volatile) organics analysis and another 77 in the liquid-liquid extractables analysis. There are compounds in the list of 109 which can be detected in both the volatiles and the extractables analyses. The EPA procedures specify that only one of these analyses is to be used for a specific compound. They do not, however, address the problem of compound recovery which may vary considerably because of matrix effects.

In the first step in the volatile organics analyses,(1,7) the organics are purged from 5 ml of water onto a trap that contains silica gel and a porous polymer, Tenax. This trap has been shown to be very efficient for trapping organics. The trapped organics are then flash heated into the gas chromatograph. The mass spectrometer continuously scans the eluting GC peaks. Identification of the specific organic compound associated with a GC peak is made by locating the proper relative intensity ratios of four key fragment ions for that compound at the correct GC retention time.(1,8) Quantification is accomplished by comparing the area of a designated ion peak specific to that compound with the area of an ion peak from an internal standard.

The semi-volatile organics are determined by liquid-liquid extraction using methylene chloride.(1,9) Two liters of water sample are extracted with methylene chloride--both at pH 11 and pH 2. These extracts, base-neutral and acid, are then concentrated 2000-fold by evaporation. An aliquot of each concentrate is then injected directly into the appropriate GC column. As with the VOA analysis, the eluting GC peaks are continuously scanned by the mass spectrometer. Compounds are identified by the relative intensity ratios of three key fragment ions and the GC retention time. The use of three key ions in this analysis versus four in the VOA is questionable since higher molecular weights are encountered and the sample itself is much more complex in character. Quantification is done as in the volatiles procedure.

Single ion chromatograms for each of the 109 listed priority pollutants must be reconstructed from the stored continuous scan mass spectrometer data to check for the presence of the pollutants. This is a time-consuming process which may take as long as the original GC/MS run itself. At least one GC/MS data system manufacturer is developing software to do this data reduction automatically and much faster than the current operator-directed data reduction process.

In analyzing the cost for the EPA analytical procedures it is helpful to treat the liquid-liquid extractables analysis alone. In Table 2 we have summarized cost estimates for Amoco Oil, the EPA, and two contractors. Contractor estimates varied from a low of $1200 to a high of just over $1500. Our costs assume approximately four hours sample preparation and 20 hours analytical time associated with the GC/MS. With an automated data reduction system that would print out an analytical report on each of the 109 compounds total GC/MS quantitation time would be near eight hours. EPA sampled API separators in their screening survey and encountered frequent emulsion problems during extraction. This led to increased sample preparation costs. Pesticides costs listed both for us and the EPA are contractor estimates.

An average cost factor of $1500 is appropriate for the total liquid-liquid extractables. With modernized GC/MS systems, costs could drop to near $800 per sample.

Total analytical costs on a per sample basis are summarized in Table 3 for us, the EPA, and two contractors. The major differences between the contractors are the costs of VOA and the liquid-liquid extractables analyses. We assume approximately eight hours per sample for the VOA. Method development and equipment modernization could lead to reduced analytical costs of near $250 for the VOA analysis.

The total analytical costs per sample, as summarized in Table 3, are close to $3000. Even with the improvements described for the liquid-liquid extractables and volatiles analyses, analytical costs on a per sample basis would still be near $2000.

Quality Assurance

Because of the likely impact of the information and the overall complexity of the analyses, a quality assurance program must be built into these procedures. The program should be designed to obtain information on both the precision and the accuracy of the determination of each specified compound. For quality control, the EPA recommends that every sixth sample be run as a spike or duplicate as a quality control device.(10) Quality assurance costs for cyanides, phenols, and asbestos were calculated on this basis. For metals, the costs are based on the same criteria and also include the frequent running of reagent blanks. Quality assurance costs are summarized in Table 4.

For more careful quantitative work in the trace organic analysis, measured amounts (at about 2X the concentration found by comparison with the internal standard) of identified pollutants in a sample should be spiked into a fresh duplicate sample. The entire procedure of both the volatile organics and liquid-liquid extractables should be repeated on the spiked sample. This procedure, although adding the cost of another complete analysis, will provide greater confidence in the quantitative results. The detection limits and the purging and extraction efficiencies can then be calculated for each of the identified pollutants in a given sample matrix.

For the volatiles analysis the EPA specifies a blank to be run along with the sample, at an added cost of $400 per analysis. As a result of the spiked samples, we have an added cost of $400 over that of the EPA and $1230 in the case of the liquid-liquid extractables analysis. EPA quality assurance costs total $1100 and our estimate falls near $2700.

Summing the refinery sampling costs on an annual basis using our Amoco estimates, an annual cost of just over $77,000 per refinery was calculated. It was assumed that four intake and four effluent samples per year would be run and that 72-hour composite samples are used in the analysis. Sampling costs were calculated to be $24,000; analytical costs, $24,800; quality assurance, $21,840; reporting costs were assumed to be near 10 percent of the total analytical cost or $7,000.

For the ten Amoco Oil refineries, a total analytical cost of $770,000 is calculated for the complete analysis. A capital charge of approximately $10,000 and an increased manpower cost of approximately $60,000 would also be incurred (since an additional professional and a technician would be required for the program). The total cost of the program for just the Amoco system approaches one million dollars--for the analytical effort alone.

These cost estimates are on the high side because they are based on a conservative analytical approach and an extensive quality assurance program. Assuming that the analytical procedures continue in development and the need for the extensive quality assurance diminishes, the costs will be reduced but by only approximately one half at most. To meet this reduced cost, sampling costs could be reduced by 1/4; analytical procedural costs could be reduced by 1/2 with a fully automated data system; and quality assurance costs could be reduced by 2/3 if the methods are proven accurate. However, if problems develop, costs could also increase.

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BIOGRAPHIES

Robert F. Babcock is a Research Chemist in the Organic Analysis Group of Standard Oil Company (Indiana), specializing in Environmental Analysis. He has a B.A. degree from DePauw University and a Ph.D. in Analytical Chemistry from Indiana University. Experience includes 13 years in refinery Technical Service work and 7 years in Research and Development.

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BIOGRAPHY

Leo J. Duffy is a Research Supervisor in the Organic Chemistry Group of Standard Oil Company (Indiana). He has a B.S. degree in chemistry from John Carroll University and the M.S. degree in fuel technology and the Ph.D. degree in fuel science from Pennsylvania State University. His experience includes polymer chemistry, coal chemistry, and 10 years diversified experience in the Analytical Division of Standard Oil.

TABLE 1 "ANALYTICAL COSTS AND THE PROBLEM POLLUTANTS"

EQUIPMENT COSTS

GC/MS System	$140,000
AA with graphite furnace	20,000
Electron capture GC	10,000
TOC analyzer	10,000
UV-visible spectrophotometer	7,500
Composite sampler	4,000
Liquid sample concentrator	3,000
Assorted glassware	2,000
Analytical balance	2,000
Water purification system	2,000
Mercury flameless unit	1,000
Total	$201,500

TABLE 2 "ANALYTICAL COSTS AND THE PROBLEM POLLUTANTS"

LIQUID-LIQUID EXTRACTABLE ANALYTICAL COSTS

(per sample basis)

			Contractor	
	Amoco	EPA	1	2
Sample preparation	$ 160	$ 400	$ 70	$ 250
GC/MS				
Base-neutrals	1,200	1,000	900	440
Acid			400	370
Pesticides	(180)	(180)	180	150
Sub Total	$1,440	$1,580	$1,550	$1,210

TABLE 3 "ANALYTICAL COSTS AND THE PROBLEM POLLUTANTS"

TOTAL ANALYTICAL COSTS
(per sample basis)

	Amoco	EPA	Contractor 1	Contractor 2
Metals	$ 700	$ 530	$ 725	$ 400
Phenolics	80	80	50	28
Cyanide	80	60	50	35
Asbestos	(300)	(300)	400	140
VOA	500	400	450	190
LLE	1,440	1,580	1,550	880
	$3,100	$2,950	$3,025	$1,673

TABLE 4 "ANALYTICAL COSTS AND THE PROBLEM POLLUTANTS"

QUALITY ASSURANCE COSTS
(per sample basis)

	Amoco	EPA
Metals	$ 320	$ 320
Cyanides	20	20
Phenols	20	20
Asbestos	70	70
VOA	800	400
LLE	1,500	270
Total	$2,730	$1,100

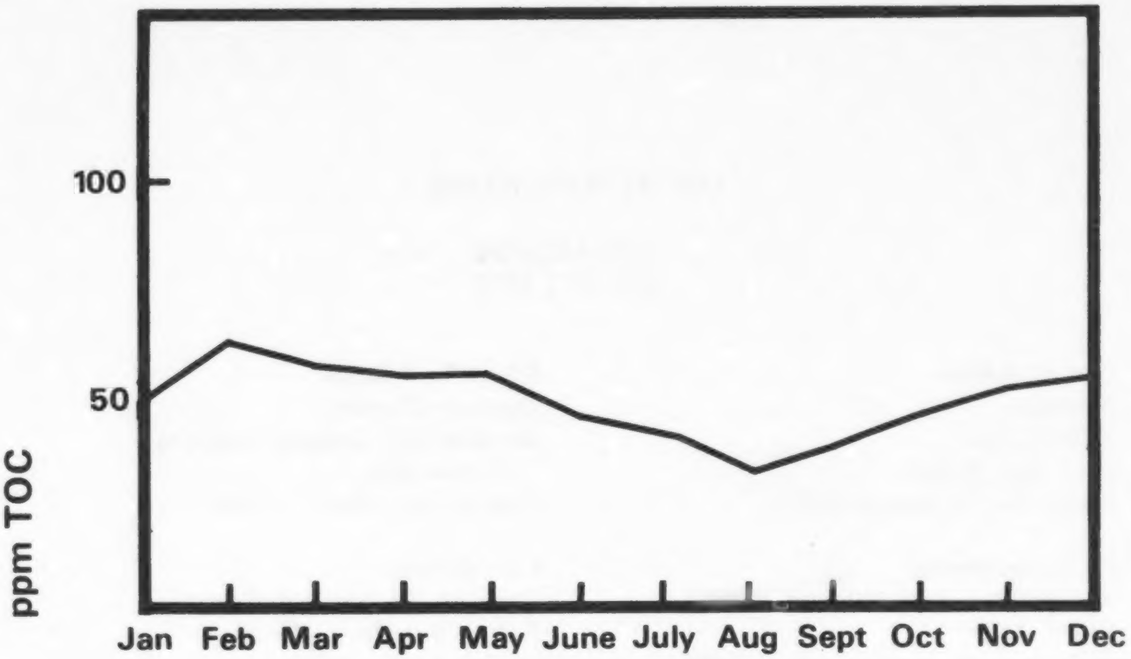

Fig 1 **Avg monthly TOC Refinery effluent**

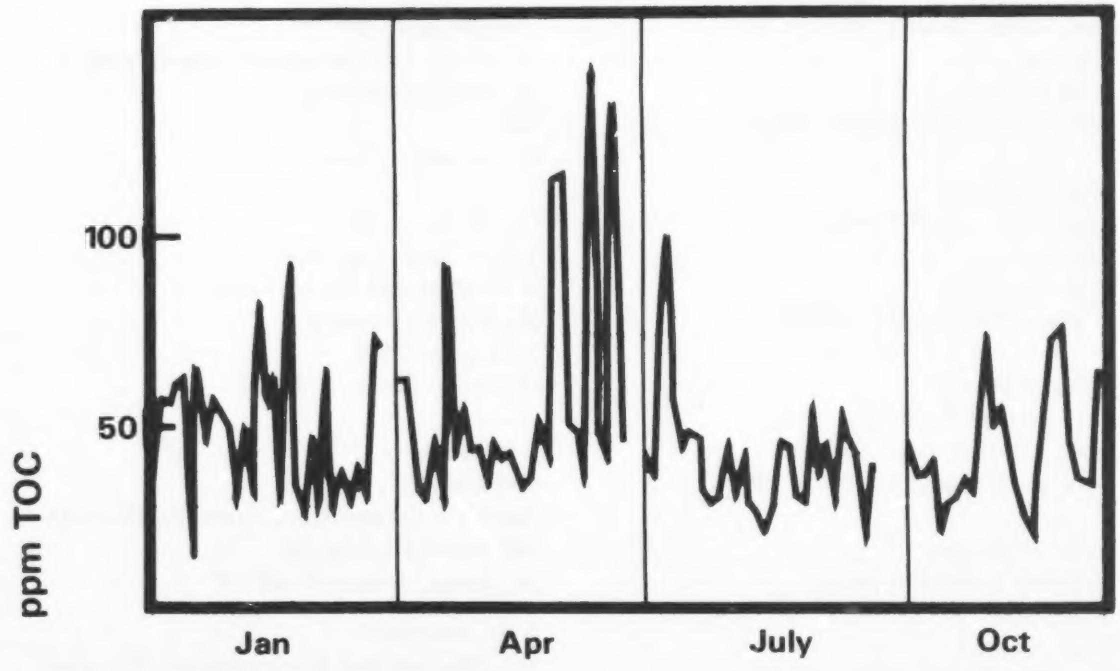

Fig 2 **Daily TOC measurements Refinery effluent**

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